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TESIS DOCTORAL:

Development of Membrane Processes for the Selective Separation of CO₂ from Biogas and Biohydrogen

Presentada por

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A mis padres:

Por su infinito amor y por soportar todas mis rebeldías.

"El hombre nunca sabe de lo que es capaz hasta que lo intenta"

— Charles Dickens

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Resumen

A pesar del notable auge de las energías renovables en los últimos años, la demanda de combustibles fósiles, fuente de energía no renovable, sigue creciendo significativamente, representado actualmente un 80% de la demanda global energética, lo que supone elevadas emisiones de gases de efecto invernadero (GEI). En aras de reducir el uso de combustibles fósiles y las emisiones de GEI, se han impulsado legislaciones que promueven la creación de un nuevo sistema energético para reemplazar a los llamados "los combustibles sucios" por energías renovables, con el fin último de mitigar el cambio climático. En este contexto, el biogás y biohidrógeno, por su naturaleza renovable y nula huella de carbono durante su combustión, son considerados dos de los biocombustibles gaseosos llamados a sustituir a los combustibles fósiles actuales.

El biogás, compuesto principalmente por CH_4 (45-85%) y CO_2 (25-50%), obtenido a partir de la degradación anaerobia de residuos orgánicos, podría ser utilizado, por ejemplo, para su exportación a la red eléctrica o redes de calefacción central de ciudades. Por su parte, el biohidrógeno se encuentra compuesto por H_2 y CO_2 mayoritariamente, cuya composición está determinada por el tipo de proceso empleado para su generación, con contenidos del 40-60% de H_2 y 47-60% de CO_2 en biorreactores de fermentación oscura de residuos orgánicos. Para que el biogás pueda ser utilizado como combustible, y ser inyectado por ejemplo en redes de gas natural, debe ser purificado y convertido en biometano de alta calidad que cumpla con los estándares regulatorios vigentes. Del mismo modo, el enriquecimiento de biohidrógeno conllevaría una remoción del CO_2, que constituye el principal contaminante de este biocombustible gaseoso.

En la actualidad, la remoción de CO_2 tanto del biogás como del hidrogeno generado a partir de gas natural a escala industrial se lleva a cabo mediante tecnologías físico/químicas, las cuales adolecen de unos altos costes de operación y problemas de corrosión. Por su parte, las tecnologías biológicas de remoción de CO_2 de biogás, como el enriquecimiento fotosintético y el enriquecimiento hidrogenotrófico, se encuentran todavía en fase de desarrollo experimental. Entre las tecnologías implementadas en la actualidad a escala industrial en la remoción de CO_2 de biogás, la separación por membranas es la única con potencial de mejora tanto en el rendimiento de separación del CO_2 del biogás y biohidrógeno, como en la reducción de costes de inversión y operación, como consecuencia de los avances que continuamente se suceden en el campo de la nanotecnología y ciencia de los materiales.

La purificación de biogás y biohidrógeno mediante membranas se basa en el principio de permeación selectiva a través de membranas semipermeables. Entre la amplia gama de

membranas de separación de gases, las membranas poliméricas se han revelado como muy competitivas, y dominan el mercado gracias a una combinación de buena procesabilidad, bajo precio, facilidad de escalado y capacidad de ajustar su composición a la aplicación buscada. Sin embargo, todavía no se ha conseguido la plena explotación a escala industrial de estas membranas debido a su falta de adecuación en algunos aspectos. Los principales retos en el campo de la tecnología de membranas son: a) la obtención de una buena selectividad sin sacrificar permeabilidad y b) el mantenimiento del rendimiento de la separación de gases a largo plazo, limitando el envejecimiento físico y la plastificación.

Con el objetivo de superar estos retos, se han introducido materiales avanzados como los Polímeros de Microporosidad Intrínseca (PIMs), Polímeros reordenados térmicamente (TR) basados en polibenzoxazoles (PBO) y se han incorporado materiales de relleno orgánicos e inorgánicos (particularmente de tamaño submicrónico y nanométrico) en una matriz polimérica para fabricar Membranas de Matriz Mixta (MMMs) con mayor selectividad y capacidad para superar los límites superiores de selectividad-permeabilidad establecidos por Robeson en sus publicaciones de 1991 y 2008 en el Journal of Membrane Science.

Dado que las membranas poliméricas tienen restricciones debido al balance ("trade-off") entre la permeabilidad y la selectividad de los gases (alta permeabilidad, baja selectividad y viceversa), esta tesis doctoral se centró en el desarrollo de una nueva tecnología de membranas para la separación de gases capaces de superar los retos de las membranas poliméricas convencionales, generando nuevas membranas con mejores propiedades de separación. La fabricación de membranas poliméricas como MMMs y MMMs modificadas por reordenamiento térmico (TR-MMMs) podría conllevar una mayor permeabilidad y selectividad en la separación de CO_2 durante el upgrading de biogás y biohidrógeno.

En el presente trabajo de tesis doctoral se fabricaron inicialmente MMMs, usando PPNs como relleno orgánico y poliamidas como matrices poliméricas para la separación de CO_2 de biogás y biohidrógeno, capaces de superar la compensación inherente entre la permeabilidad y la selectividad. En particular, se combinaron las excepcionales propiedades térmicas de los PPNs con poliamidas reordenables térmicamente para investigar las propiedades de transporte en TR-MMMs. En primer lugar, se llevó a cabo una evaluación sistemática de las propiedades de permeabilidad al gas CO_2 y CH_4 de estas MMMs y TR-MMMs. Para tal efecto, se sintetizó una hidroxi-poliamida (HPA, 6FCl-APAF) con alto peso molecular utilizada como matriz polimérica para la fabricación de MMMs usando PPN-2 (tripticeno- trifluoroacetofenona) como relleno al 10, 15, 20, 30 y 40% en peso. Adicionalmente, las MMMs preparadas fueron sometidas a un tratamiento térmico, para

inducir el reordenamiento de la HPA a un polibenzoxazol (β-TR-PBO) y obtener las correspondientes TR-MMM. Para caracterizar completamente los polímeros, se requirió de la combinación de información procedente de múltiples técnicas físico-químicas para dilucidar la estructura de los materiales investigados y establecer los límites de la estabilidad térmica, la estructura y las condiciones para el posterior procesamiento del material. En este estudio se midió la permeabilidad para gases puros (N_2, O_2, CH_4 y CO_2) a 35 °C y 3 bares en un equipo de permeación de volumen-constante presión-variable, obteniendo con estas medidas la selectividad ideal para los pares de gases, CO_2/CH_4, CO_2/N_2 y O_2/N_2. Se observó un incremento en la permeabilidad de las MMMs respecto a la matriz polimérica para todos los gases, a medida que se incrementó el contenido de PPN. La mejora en la permeabilidad de las TR-MMMs (β-TR-PBO basadas en HPA) fue considerablemente mayor que el incremento en las MMMs. En el caso particular de las membranas cargadas con un 30% de PPN, las permeabilidades al CO_2 y CH_4, tanto antes como después de la reordenación térmica, aumentaron hasta alcanzar el límite superior de Robeson 2008. Estas permeabilidades relativamente buenas fueron atribuidas (entre otras causas) a la buena interacción partícula-matriz, generando membranas libres de huecos interfaciales. Sin embargo, este incremento de permeabilidad no se observó para la MMMs cargada con 40% de PPN. La disminución de permeabilidad al 40% se atribuyó a la formación de huecos interfaciales generados por la aglomeración de las partículas. La selectividad CO_2/CH_4 de las MMMs, así como de las TR-MMMs, disminuyó ligeramente tanto cuando se aumentó la carga de PPN como cuando se produjo el reordenamiento térmico.

Con base en los resultados obtenidos en la primera parte de la investigación, la carga óptima para esta matriz polimérica, 6FCl-APAF, se estableció en el 30% en peso de PPNs. El potencial de estas membranas para separación de H_2 se evaluó determinando la permselectividad del hidrógeno frente al CH_4, CO_2 y N_2 en las MMMs y a sus correspondientes TR-MMM, bajo las mismas condiciones de operación. Se observó un notable incremento en las propiedades de permeabilidad y selectividad para los pares de gases H_2/N_2 y He/CH_4 con membranas cargadas al 30% en comparación con la matriz polimérica y la cargada al 20%. El mismo comportamiento se observó en las TR-MMM, aunque con una ligera disminución en la selectividad. A pesar de que para el par de gas H_2/CO_2 (de mayor importancia en este trabajo de investigación) no se obtuvieron los resultados esperados, conduciendo a una selectividad cercana a 1 para el caso de las membranas TR-MMM, se pudo apreciar una notable mejoría en comparación con membranas convencionales para separación de H_2 no sometidas a reordenamiento térmico. El comportamiento único de las

membranas evaluadas en el transporte de gases demuestra las ventajas del PPN como relleno de una membrana de separación de gases para la posible separación y purificación de H_2 y la captura de CO_2.

Con el objetivo de completar esta tesis doctoral, se llevó a cabo la síntesis y ensayos de nuevos materiales, que contienen grupos *m*-Terfenilo, usados como matrices poliméricas en la fabricación de MMMs. Se sintetizó una hidroxipoliamida (HPA), una poliamida (PA) y un copolímero (Co-HPA-PA), producido por copolimerización estequiométrica de las diaminas APAF y 6FpDA y usando como cloruro de ácido 5'-terc butilo-*m*-terfenilo-4,4''-dicarboxílico (tBTpCl) para todas las síntesis realizadas. Las MMMs se cargaron al 20% en peso de PPNs; empleando el PPN-2 utilizado previamente y un nuevo material de relleno PPN-1, formado a partir de isatina y tripticeno. Las membranas obtenidas fueron sometidas a un tratamiento térmico para convertir la HPA en polibenzoxazol para obtener así las TR-MMMs y evaluar las propiedades se separación de gases para H_2, N_2, O_2, CH_4 y CO_2 a 35 °C y 3 bares, siguiendo las mismas condiciones de operación que en los trabajos anteriores. En comparación con las matrices poliméricas, tanto el reordenamiento térmico como la adición de PPNs aumentaron la permeabilidad con ligeras disminuciones de la selectividad para todos los gases probados. El compromiso de permeabilidad frente a la selectividad arrojó excelentes resultados, especialmente para el par de gases H_2/CH_4 y H_2/N_2, acercándose al límite de Robeson 2008. Se realizó, además, una comparativa de propiedades de transporte utilizando PPN-1 y PPN-2, observando que las mejores propiedades de separación de gases se obtuvieron con el uso de PPN-2 como relleno, lo que se atribuyó a una mejor interacción polímero-relleno. Se llevó a cabo la caracterización de la permeabilidad al gas en función de la distancia intersegmental de la cadena, esta última obtenida mediante la técnica de difracción de rayos X de ángulo ancho (WAXD), y la fracción de volumen libre de la membrana junto con los diámetros cinéticos de los gases permeados. Se observó que tras el proceso de reordenamiento térmico y al introducir PPNs en la cadena de la columna vertebral de las poliamidas, se incrementaba el espacio *d*, lo que condujo a un aumento de la permeabilidad del gas debido al aumento de la distancia intersegmental. Se observó además que la selectividad no se vio notablemente afectada probablemente debido al aumento de la rigidez de las cadenas. En términos de volumen libre, la permeabilidad siguió una tendencia exponencial frente al volumen libre y la función cuadrática del diámetro cinético del gas. La combinación de una poliamida con alta permeabilidad al H_2 y PPNs para conferir al material alta selectividad H_2/CH_4 y H_2/N_2 dio lugar a membranas compuestas que superan la limitación de rendimiento de las membranas poliméricas puras.

En este trabajo de tesis se demostró que, al igual que en el caso de las MMMs, cambios sutiles en la química del polímero, así como en los rellenos, pueden tener efectos importantes en las interacciones polímero-relleno y en las propiedades de los TR-MMM, tanto antes como después de la reordenación térmica. Se demostró, además, que los materiales nanoporosos avanzados que se están explorando actualmente como rellenos en las MMMs, también pueden aplicarse para mejorar el rendimiento de separación de gases de los polímeros aptos para producir benzoxazoles, siguiendo la misma estrategia en MMMs.

Abstract

Despite the boom in renewable energies occurred in recent years, the demand for fossil fuels, a non-renewable energy source, continues to grow steadily. Indeed, fossil fuels currently accounts for 80% of global energy demand, which entails high greenhouse gas (GHG) emissions. In order to reduce the use of fossil fuels and GHG emissions, regulations have been introduced to promote the creation of a new energy system to replace the so-called "dirty fuels" with renewable energies, with the ultimate goal of mitigating climate change. In this context, biogas and biohydrogen, due to their renewable nature and zero carbon footprint during combustion, are considered two of the gaseous biofuels that will replace current fossil fuels.

Biogas from the anaerobic degradation of organic waste, composed mainly of CH_4 (45-85%) and CO_2 (25-50%), could be used as an energy feedstock to export energy to the electricity grid or central heating networks of cities. On the other hand, biohydrogen is composed mainly of H_2 and CO_2, whose composition is determined by the type of generation process, with contents of 40-60% of H_2 and 47-60% of CO_2 in bioreactors for dark fermentation of organic waste. Biogas must be purified and converted into high quality biomethane meeting current regulatory standards prior use as a vehicle fuel or injection into natural gas networks. Likewise, the enrichment of biohydrogen requires the removal of CO_2, which is the main pollutant of this gaseous biofuel.

Currently, the removal of CO_2 from both biogas and hydrogen generated from natural gas on an industrial scale is carried out by means of physical/chemical technologies, which suffer from high operating costs and corrosion problems. Biological technologies for CO_2 removal from biogas, such as photosynthetic enrichment and hydrogenotrophic enrichment, are still in the experimental development phase. Among the technologies currently implemented on an industrial scale for the removal of CO_2 from biogas, membrane separation is the only one with the potential to improve the performance of CO_2 separation from both biogas and biohydrogen, and to reduce investment and operating costs, as a result of the current advances in the field of nanotechnology and materials science.

Membrane purification of biogas and biohydrogen is based on the principle of selective permeation through semi-permeable membranes. Among the broad range of membranes for gas separation, polymeric membranes have proved to be very competitive, and dominate the market due to a combination of good processability, low price, ease of scale-up and ability to adjust their composition to the target application. However, full industrial-scale exploitation of these membranes has not yet been achieved. The main

challenges in the field of membrane technology are a) obtaining good selectivity without sacrificing permeability and b) maintaining long-term gas separation performance by limiting physical aging and plasticization.

In order to overcome these challenges, advanced materials such as Polymers of Intrinsic Microporosity (PIMs), Thermally Rearranged (TR) polymers based on polybenzoxazoles (PBO) and organic and inorganic fillers (particularly of submicron and nanometer size) incorporated into a polymeric matrix to manufacture Mixed Matrix Membranes (MMMs) with enhanced membrane selectivity and higher capacity to exceed the selectivity-permeability upper limits established by Robeson in his 1991 and 2008 publications in the Journal of Membrane Science.

Since polymeric membranes have restrictions due to the trade-off between gas permeability and selectivity (high permeability, low selectivity and vice versa), this PhD thesis focused on the development of a new membrane technology for gas separation capable of overcoming the challenges of conventional polymeric membranes, generating new membranes with improved separation properties. The manufacture of polymeric membranes such as MMMs and thermal rearrangement modified MMMs (TR-MMMs) could lead to higher permeability and selectivity in CO_2 separation during biogas and biohydrogen upgrading.

In this PhD thesis, MMMs were initially fabricated, using PPNs as organic fillers and polyamides as polymeric matrices for the separation of CO_2 from biogas and biohydrogen, capable of overcoming the inherent trade-off between permeability and selectivity. In particular, the exceptional thermal properties of PPNs were combined with thermally rearrangeable polyamides to investigate the transport properties in TR-MMMs. First, a systematic evaluation of the CO_2 and CH_4 gas permeability properties of these MMMs and TR-MMMs was carried out. For this purpose, a hydroxy-polyamide (HPA, 6FCl-APAF) with high molecular weight was synthesized and used as a polymeric matrix for the manufacture of MMMs using PPN-2 (trypticene- trifluoroacetophenone) as filler at 10, 15, 20, 30 and 40% (on weight basis). Additionally, the prepared MMMs were subjected to heat treatment to induce HPA rearrangement to a polybenzoxazole (β-TR-PBO) and obtain the corresponding TR-MMMs. To fully characterize the polymers, the combination of information from multiple physicochemical techniques was required to elucidate the structure of the investigated materials and to establish the limits of thermal stability, structure, and conditions for further processing of the material. In this study, membrane permeability for pure gases (N_2, O_2, CH_4 and CO_2) was measured at 35 °C and 3 bar in a constant-volume

pressure-variable permeation apparatus, obtaining with these measurements the ideal selectivity for the gas pairs CO_2/CH_4, CO_2/N_2 and O_2/N_2. An increase in the permeability of the MMMs with respect to the polymer matrix was observed for all gases as the PPN content increased. The improvement in the permeability of TR-MMMs (β-TR-PBO based on HPA) was considerably greater than the increase in MMMs. In the particular case of membranes loaded with 30% PPN, the permeabilities to CO_2 and CH_4, both before and after thermal rearrangement, increased to reach the 2008 Robeson upper bound. These relatively good permeabilities were attributed (among other causes) to good particle-matrix interaction, generating membranes free of interfacial voids. However, this increase in permeability was not observed for MMMs loaded with 40% PPN. The decrease in permeability at 40% was attributed to the formation of interfacial voids generated by particle agglomeration. The CO_2/CH_4 selectivity of MMMs, as well as TR-MMMs, decreased slightly both when PPN loading was increased and when thermal rearrangement occurred.

Based on the results obtained in the first part of this PhD Thesis, the optimum loading for this polymeric matrix, 6FCl-APAF, was set at 30% of PPNs. The potential of these membranes for H_2 separation was evaluated by determining the permselectivity of hydrogen to CH_4, CO_2 and N_2 in the MMMs and their corresponding TR-MMMs, under the same operating conditions. A remarkable increase in permeability and selectivity properties was observed for H_2/N_2 and He/CH_4 gas pairs with 30% loaded membranes compared to polymer matrix and 20% loaded membranes. The same behavior was observed in the TR-MMMs, although with a slight decrease in selectivity. Although the expected results were not obtained for the H_2/CO_2 gas pair (of major importance in this research work), leading to a selectivity close to 1 for the case of TR-MMM membranes, a remarkable improvement could be appreciated in comparison with conventional membranes for H_2 separation not subjected to thermal rearrangement. The unique gas transport behavior of the evaluated membranes demonstrates the advantages of PPN as gas separation membrane filler for the potential separation and purification of H_2 and CO_2 capture.

Finally, the synthesis and testing of new materials, containing *m*-Terphenyl groups, used as polymeric matrices in the manufacture of MMMs, was carried out. A hydroxypolyamide (HPA), a polyamide (PA) and a copolymer (Co-HPA-PA), produced by stoichiometric copolymerization of the diamines APAF and 6FpDA and using 5'-tert-butyl-*m*-terphenyl-4,4''-dicarboxylic acid chloride (tBTpCl) for all syntheses performed were synthesized. The MMMs were loaded to 20% of PPNs, using the previously used PPN-2 and a new filler material PPN-1, formed from isatin and trypticene. The membranes obtained

were subjected to heat treatment to convert HPA to polybenzoxazole to obtain TR-MMMs and to evaluate the gas separation properties for H_2, N_2, O_2, CH_4 and CO_2 at 35 °C and 3 bar, following the same operating conditions as in the previous work. Compared to the polymeric matrices, both thermal rearrangement and the addition of PPNs increased permeability with slight decreases in selectivity for all gases tested. The trade-off of permeability versus selectivity yielded excellent results, especially for the H_2/CH_4 and H_2/N_2 gas pair, approaching the 2008 Robeson upper bound. A comparison of transport properties using PPN-1 and PPN-2 was also carried out, observing that the best gas separation properties were obtained with the use of PPN-2 as filler, which was attributed to a better polymer-filler interaction. Characterization of gas permeability as a function of intersegmental chain distance, the latter obtained by wide-angle X-ray diffraction (WAXD), and membrane free volume fraction together with kinetic diameters of permeated gases, was carried out. It was observed that after the thermal rearrangement process and by introducing PPNs into the polyamide backbone chain, the *d*-spacing was increased, leading to an increase in gas permeability due to the increase in intersegmental distance. It was also observed that the selectivity was not noticeably affected probably due to the increased stiffness of the chains. In terms of free volume, permeability followed an exponential trend versus free volume and the quadratic function of the kinetic gas diameter. The combination of a polyamide with high H_2 permeability and PPNs to confer high H_2/CH_4 and H_2/N_2 selectivity to the material, resulted in composite membranes that overcome the performance limitation of pure polymeric membranes.

In this thesis work, it was shown that, as in the case of MMMs, subtle changes in polymer chemistry as well as fillers can have important effects on the polymer-filler interactions and properties of TR-MMMs, both before and after thermal rearrangement. It was further demonstrated that advanced nanoporous materials currently being explored as fillers in MMMs can also be applied to improve the gas separation performance of polymers suitable for producing benzoxazoles, following the same strategy in MMMs.

Articles included in this Thesis

C. Soto, C. Aguilar Lugo, S. Rodriguez, L. Palacio, Á. E. Lozano, P. Prádanos, A. Hernández. *Enhancement of CO₂/CH₄ permselectivity via thermal rearrangement of mixed matrix membranes made from an o-hydroxy polyamide with an optimal load of a porous polymer network.* Separation and Purification Technology (2020). 247:116895. DOI: 10.1016/j.seppur.2020.116895.

Cenit Soto, Edwin S. Torres-Cuevas, Alfonso González-Ortega, Laura Palacio, Ángel E. Lozano, Benny D. Freeman, Pedro Prádanos and Antonio Hernández. *Gas Separation by Mixed Matrix Membranes with Porous Organic Polymer Inclusions within o-Hydroxypolyamides Containing m-Terphenyl Moieties.* *Polymers* (2021), *13*(6), 931; DOI: https://doi.org/10.3390/polym13060931.

Cenit Soto, Edwin S. Torres-Cuevas, Alfonso González-Ortega, Laura Palacio, Pedro Prádanos, Benny D. Freeman, Ángel E. Lozano, Antonio Hernández. *Hydrogen Recovery by Mixed Matrix Membranes Made from 6FCl-APAF HPA with Different Contents of a Porous Polymer Network and Their Thermal Rearrangement.* Polymers (2021), 13(24), 4343. DOI: https://doi.org/10.3390/polym13244343.

Cenit Soto, Edwin S. Torres-Cuevas, Laura Palacio, Pedro Prádanos, Benny D. Freeman, Ángel E. Lozano, Antonio Hernández, Bibiana Comesaña-Gándara. *Gas Permeability, Fractional Free Volume and Molecular Kinetic Diameters: The Effect of Thermal Rearrangement on ortho-hydroxy Polyamide Membranes Loaded with a Porous Polymer Network.* Membranes (2022), 12(2), 200. DOI: https://doi.org/10.3390/membranes12020200.

Chapter 1

Introduction

1.1 The challenge of climate change

The last Assessment Report (AR5, 2014) of the Intergovernmental Panel on Climate Change (IPCC) concluded that the Earth warming observed since pre-industrial era is mainly caused by anthropogenic activities, which is resulting in a potentially negative impact of climate change (Intergovernmental Panel on Climate Change, 2015). Indeed, climate change due to global warming is likely the most important environmental challenge of this XXI century, with severe negative social and economic consequences. From 1906 to 2005, the Earth's surface temperature has increased 0.9 ℃ (Lenssen et al., 2019). Similarly, global warming is likely to cause an increase of 1.5 °C between 2030 and 2052, as a result of the increased Greenhouse Gas Emissions (GHG) into the atmosphere, which block heat from escaping from Earth. In this context, the Working Group I recently published the first instalment of the IPCC's Sixth Assessment Report (AR6) that will be completed by late 2022 or early 2023 to serve as a methodology for use by parties to the United Nations Framework Convention on Climate Change (UNFCCC) before the 2023 Global Stock take (IPCC, 2021) (Last access 11/08/2021). This report showed that the emissions of GHG from human activities were the responsible for approximately 1.1 ℃ of warming since 1850-1900, and finds that averaged over the next 20 years, global temperature is expected 1.5 ℃ of warming.

Carbon dioxide (CO_2) is the most relevant GHG, which is produced naturally by respiration and volcanic eruptions and anthropogenically by fossil fuels burning and deforestation, etc. CO_2 is used as reference of Global Warming Potential (GWP) and represents 76% of the total GHG emission worldwide (Intergovernmental Panel on Climate Change, 2015). The second most important GHG is methane (CH_4), with a GWP of 23 times higher than CO_2. CH_4 is a hydrocarbon produced naturally from organic matter fermentation and by anthropogenic activities such as intensive agriculture, natural gas processing, ruminants farming and waste treatment (Shine et al., 2005). Nitrous Oxide (N_2O), with a GWP 296 times higher than CO_2, is produced during intensive agriculture and in chemical industry, and represents 6% of the total GHG emissions (Shine et al., 2005) (Figure 1).
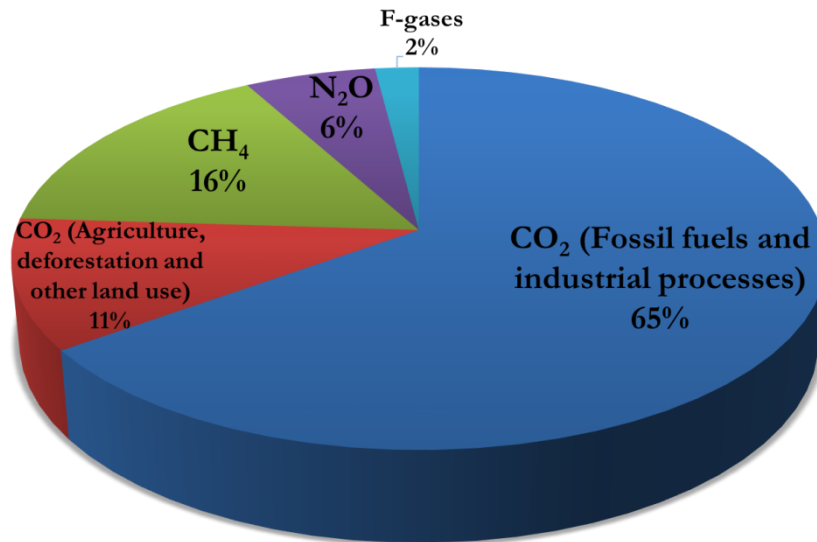
Figure 1. IPCC 2014 Global greenhouse gas emissions shares in 2010.

GHG emissions are mainly caused by economic sectors such as the energy production from fossil fuels, Agriculture Forestry and Other Land Use (AFOLU), and industry. Anthropogenic GHG emissions in 2010 were discharged mainly by 10 countries, which produced about 70% of CO_2 emissions from fossil fuels and industry. In 2018, energy generation accounted for 33.1 gigatons (Gt) of CO_2 emissions, with coal-fired power plants generating 10 Gt CO_2 (an increase of 2.9% compared with 2017 levels), mainly in Asia. Although countries such as China, India and the United States accounted for 85% of the net increase in emissions between 2017 and 2018, 215 Mt of emissions were avoided due to the increased use of renewable energy in the energy sector.

In 2018, the IPCC special report "Global warming of 1.5 ℃" highlighted that global warming must not exceed 2 °C, and human beings must do everything possible to limit this increase to 1.5 °C. GHG emissions will need to be kept at 25-30 Gt CO_2e year^{-1} in 2030. However, these emissions will never decrease without phasing out coal in the energy sector and concomitantly increasing the amount of energy produced from renewable sources, the electrification of transportation and the reduction of the "carbon footprint" of the current food system. The last United Nations Climate Conference (COP24-2018) adopted the Katowice package, which contains detailed common rules, guidelines and procedures implementing the Paris Agreement, which aims to limit global warming to 1.5 °C and strengthen the capacity of countries to cope with the effects of climate change. In addition, the Working Group II to the Sixth Assessment Report of the IPCC, that will be also published by late 2022 or early 2023, will reveal that climate-resilient development will not

be possible if global warming increases by more than 2 °C, thus highlighting the need to reduce the temperature increase to 1.5°C.

The European Union (EU) has been at the forefront of international efforts to combat climate change, playing a global leadership role in the promotion of renewable energies. In this context, the EU has launched the European Green Deal, which includes the need to drastically reduce polluting emissions, to combat climate change, to a minimum of 55% by 2030 and to be the first climate-neutral continent by 2050. The Spanish Government has recently approved the "Climate Change and Energy Transition Law", aiming at achieving carbon neutrality before 2050 (emitting only the GHGs that can be absorbed by Spanish forests). This regulation has set intermediate goals in 2030 such as reducing by 23% the GHGs emissions compared to 1990, reaching up to 42% of renewable energy use and producing 74% of electricity from renewable energies (BOE, 2021).

1.2. The role of Biogas and Biohydrogen on climate change mitigation

Biogas is produced via Anaerobic Digestion (AD) of residual biomass from diverse origins such as urban solid waste, livestock waste, agricultural waste, and wastewater. Anaerobic digestion is a biological process (based on the action of micro-organisms) able to convert this residual biomass, by means of oxidations and reductions of organic carbon, to carbon dioxide (CO_2) and methane (CH_4) in the absence of oxygen (Andriani et al., 2014) (Kougias and Angelidaki, 2018). This biological conversion is carried out through a sequence of hydrolysis, acidogenesis, acetogenesis and methanogenesis steps in an anaerobic digester (Q. Zhang et al., 2016). Biogas is typically composed of CH_4 and CO_2 in a concentration range of 45-85% and 25-50%, respectively, and minor concentrations of other components such as water (H_2O; 5-10%), nitrogen (N_2; ~0-1%), oxygen (O_2; ~0-0.5%), hydrogen sulfide (H_2S; 0-10000 ppm), ammonia (NH_3; 0–100 ppm), hydrocarbons (0–200 mg Nm^{-3}) (EBA 2020) (Toledo-Cervantes et al., 2017). The biogas produced by AD represents an excellent alternative to fossil-based energy vectors (Kougias and Angelidaki, 2018), since biogas can be used for the generation of heat, steam and electricity, as a substrate in fuel cells, as a substitute of natural gas for domestic and industrial use or as a vehicle fuel (Andriani et al., 2014). The contribution of biogas in the European Union could account for 10% of the natural gas demand by 2030 and up to 30-40% by 2050.

Based on to the latest report of the World Biogas Association (WBA 2019), 50 million micro-scale digesters generating biogas for cooking or heating were in operation, mainly in China (42 million) and India (4.9 million). On the other hand, 18,774 large-scale plants devoted to generating 11 GW (a biomethane plant produces an average of 36 GWh per year)

of electricity were in operation in 2021 in Europe, Germany being the leader in the European market with 11,269 plants in 2020 Germany being the leader in the European market with 11,279 in 2020 plants (140 plants/ 1 Mio capita), followed by Italy (1,666 in 2020) and France (833 new plants in 2020) (last access 11/07/2021) (EBA 2020)(EBA 2021). China with 6,972 large scale digesters and USA with 2200 AD plants in 2015 represented the second and third largest biogas producer in the world. The global electricity generation from biogas increased by 90% in six years (from 46,108 GWh in 2010 to 87,500 GWh in 2016) and by 11.5% from 2016 to 2020 (from 87,500 GWh in 2016 to 96,565 GWh in 2020) (WBA, 2019)("IRENA 2022") (last access 11/07/2021).

Biogas can be purified and converted into a high quality biomethane via three sequential processes: desulfurization (elimination of the H_2S), CO_2 removal and biomethane polishing (removal of the minor biogas contaminants) (Angelidaki et al., 2018). The European Standard (EN-16723) for biomethane injection into natural gas grids (UNE-EN 16723-1-2016) and automotive/vehicle fuel (UNE-EN 16723-2-2017) requires an effective cleaning of biogas. This UNE-EN 16723-1-2016 standard has resulted in a specific Spanish standard for biomethane injection into natural gas grid requiring a minimum methane content of 90% and a maximum CO_2 content of 2% (v/v). (BOE 2018) (last access 09/08/2021) (BOE 2018). In 2017, the number of biogas upgrading plants in the world accounted for 700 plants, Europe being the leading region with 540 upgrading plants in operation. At the end of 2020 (the most recent data available), 880 biogas upgrading plants with a production capacity of 2.43 billion m^3 were in operation in Europe (161 additional plants relative to 2019)(EBA 2020)(EBA 2021). By 2021 the increase in the number of biomethane plants is expected to be even faster since 115 plants have started operation by August 2021 (EBA 2021).

On the other hand, biologically produced hydrogen (commonly referred as biohydrogen) generated via Dark Fermentation (DF) represents another alternative bioenergy source (Bakonyi et al., 2013b). Biohydrogen (bioH_2) has the potential to gradually become a major hydrogen generating technology for future development of a green economy (Ramírez-Morales et al., 2015). In this context, hydrogen has multiple advantages as a clean energy vector such as : (i) the combustion of H_2 gas can be pollution-free in fuel cells, (ii) its energy efficiency in hydrogen fuel cells is ~50% higher than that of gasoline, (iii) has a high energy yield of 122 kJ/g, which is 2.75-fold greater than that from hydrocarbon fuels on a mass basis, (iv) its conversion efficiency to electricity could be doubled using fuel cells instead of gas turbines, and finally (v) can be stored as a metal hydride.

Dark fermentation is based on hydrogen and carbon dioxide (CO_2) production via anaerobic bacteria (Rittmann and Herwig, 2012) and/or algae growing in the absence of light and with high carbohydrate content as substrate (Das and Veziroglu, 2008)(Bharathiraja et al., 2016). The biohydrogen produced is mainly composed of hydrogen (40-60%) and carbon dioxide (47-60%) with traces of methane and H_2S (Ramírez-Morales et al., 2013) (IEA, 2019). Currently, only 1% of de hydrogen is produced from biomass (Bharathiraja et al., 2016). This fact is probably due to the relatively late research on $bioH_2$ production by dark fermentation, where research is still conducted at a laboratory scale with a limited number of experiments at pilot scale (Tapia-Venegas et al., 2015). Despite the fact that the H_2 yield from dark fermentation is higher than that of other processes, the main disadvantage of the gas generated during dark fermentation is its low hydrogen concentration (40–60%; v/v) (Mona et al., 2020), which hinders its direct use in fuel cells for electricity generation (where the purity of hydrogen is crucial to achieve high energy yields) (Ramírez-Morales et al., 2013). Therefore, it is crucial to separate H_2 from the multiple gas by-products from DF, mainly CO_2, in order to obtain purified hydrogen. For instance, a hydrogen content of 73% can be obtained in a two-step gas membrane separation process (Mona et al., 2020).

The sustained use of non-polluting renewable energy vector such as biogas and biohydrogen is needed to reduce the consumption and dependence from fossil fuels (Elbeshbishy et al., 2017). According to the International Energy Agency, the share of renewable and low-carbon transport fuels should increase up to 6.8% in 2030 in Europe, with advanced biofuels representing at least 3.6% of the total fuel consumption. The development of compact and low-cost technologies for the conversion of biogas to high-purity biomethane and biohydrogen to pure H_2 is crucial to ensure the competitiveness of these green gas vectors as an energy source.

1.3. Biogas and biohydrogen purification technologies

Nowadays, there are two main types of technologies for biogas purification, physicochemical and biological methods, while biohydrogen purification is only performed by physicochemical methods. Physicochemical technologies exhibit high energy and chemical requirements, which increases the operating cost and environmental impacts. As an example, this section will only focus on CO_2 removal technologies.

Pressure swing adsorption (PSA), cryogenic CO_2 separation, scrubbing with water, organic solvents or chemical solutions, and membrane separation, dominate the biogas upgrading market nowadays (Muñoz et al., 2015), while PSA, cryogenic distillation and

membrane separation are the most popular technologies for hydrogen purification at commercial scale (Liemberger et al., 2017) (Hinchliffe and Porter, 2000) (Ockwig and Nenoff, 2007).

Pressure Swing adsorption

The process is divided in several steps, mainly: (i) adsorption, (ii) co-current depressurization, (iii) countercurrent depressurization, (iv) purge, and (v) countercurrent pressurization (Adhikari and Fernando, 2006). Initially, the impurities of the biogas and bioH$_2$ are adsorbed by a packed bed column using a solid adsorbent (zeolites, activated carbon, silica, or alumina gel depending on the application) at high pressure with a limited adsorption of CH$_4$ and H$_2$. The components adsorbed are stripped out from the solid by lowering the pressure and purging the impurities with a part of the previously purified gas (therefore the adsorbent can be reused) (Sircar and Golden, 2009). PSA is based on multiple columns (up to twelve) to ensure a continuous separation process and to obtain the desired purity at 20-40 bar for bioH$_2$ or 4-10 bar for biogas (Muñoz et al., 2015) (Liemberger et al., 2017). The main disadvantage of the PSA process derives from the high cost of the compression of the inlet gas. In addition, this technology requires a large footprint at full scale operation (Al-Mufachi et al., 2015). The main advantages of PSA is its ability to reduce undesired impurities to parts per million (ppm), achieving 99.9999 % and 96-98% of purity and with recoveries of 70-95% and 98% for hydrogen and biogas, respectively (Sircar and Golden, 2009). In this context, hydrogen or methane recovery in PSA is influenced by factors such as the inlet hydrogen or methane concentrations, gas impurities and inlet and purge pressure (Adhikari and Fernando, 2006). Until 2019, about 85% of the hydrogen produced worldwide was upgraded by PSA, which renders this technology the most used industrial process for hydrogen purification (Schorer et al., 2019).

Cryogenic distillation

This low-temperature separation process uses the difference in boiling temperatures of the components of the gas mixture (either biogas or biohydrogen). For instance, hydrogen separation by cryogenic distillation is carried out by cooling the gas mixture below -150 ºC (Voldsund et al., 2016). Therefore, cryogenic distillation takes advantage of the low boiling point of hydrogen (at -252.9 ºC) compared to the rest of biohydrogen components, which condense to form a liquid phase while hydrogen remains in the gas phase (Al-Mufachi et al., 2015). The condensation of impurities such as hydrocarbons in tail gas is typically carried out

by Joule-Thompson cooling, which is more efficient when the operating pressure is low, hydrogen content is lower than 40% and the concentration of easily condensable components is high. Purities between 90-95% can be achieved with recoveries of 90-95% (Peramanu et al., 1999). On the other hand, biogas upgrading via cryogenic distillation is performed at ~10 bar via a stepwise decrease in temperature to -25 °C (to condensate water, H_2S, siloxanes and halogens), to -55 °C (to condensate CO_2) and finally to -85 °C as polishing step (Ryckebosch et al., 2011). The use of a high pressure prevents CO_2 solidification below -78 °C, which avoids operational problems caused by clogging of pipelines and heat exchangers. This technology typically reaches CH_4 contents over 97% in the upgraded biogas, with methane losses lower than 2%. However, cryogenic separation exhibits high operating costs as a result of its high energy demand caused by the extreme gas cooling processes and high operational pressures (Schorer et al., 2019).

Water Scrubbing

Water scrubbing is the most common operational unit for biogas upgrading, but it has not been used for hydrogen purification. This process is based on the use of water as absorbent to preferentially remove CO_2 and H_2S from biogas due to their higher solubility compared to CH_4 (Angelidaki et al., 2018). The pressurized biogas (6–10 bar) is injected into the bottom of a scrubber column, while water is provided from the top of the column using high pressure water pump (Angelidaki et al., 2018)(Bauer et al., 2013). The packing material used in the scrubbing column to increase the gas-liquid mass transfer is usually a random material. The biomethane is released from the top of the scrubber, while the water phase containing CO_2 and H_2S is pumped into a flash unit operating at 2-4 bar, which releases part of the CO_2 and most of the CH_4 dissolved (80-90% and 10-20% respectively).

The water phase is pumped into a final stripping column operated with air at atmospheric pressure, where water is regenerated and returned to the initial scrubbing column (Muñoz et al., 2015). However, the low solubility and diffusivity of CO_2 in water entails a slow CO_2 absorption in water, and therefore long retention times in the scrubbing column are required. This ultimately results in large volumes of the scrubbing columns to obtain high biomethane purities. In addition, the increase in CO_2 solubility requires high biogas and water pressures, which entails high operating and capital costs (Bauer et al., 2013)(Andriani et al., 2014).

Membrane separation

Separation of gas mixtures through membranes has become a relevant unitary operation for the recovery of valuable gases and mitigation of atmospheric pollution, which offers several advantages over conventional gas separation methods (Sridhar et al., 2007). Indeed, Membrane Separation (MS) is considered nowadays the most promising gas purification technology. Membrane separation technology is based on the interaction (physical or chemical) of certain gases with the membrane material (Ismail et al., 2015). The membranes used are selective physical barriers to certain components that permeate across them (Adhikari and Fernando, 2006). Gas separation by membrane technology is characterized by flux and selectivity properties, which provide functional transport of the target gases across the barrier (permeability). This technology presents a low energy consumption, a simple operation, cost effectiveness, smaller carbon footprint, a negligible chemical consumption and low environmental impacts (Chen and Chung, 2012) (Sridhar et al., 2014). The potential of MS to achieve high efficiencies of gas separation makes it attractive for different industrial applications including refineries and chemical industries, and recent advances in material science render MS into a competitive technology (Bernardo et al., 2009). Today, the use of membranes in industry includes the separation of nitrogen or oxygen from air, separation of H_2 from gases such as CH_4, separation of CH_4 from biogas, removal of CO_2 and H_2S from natural gas, etc. The use of membranes in separation processes is rapidly growing, especially in Europe (Figure 2). Among the available technologies for the purification of biogas to biomethane, membrane separation is currently the most widely used technology (39%), followed by water scrubbing (22%) and chemical scrubbing (18%). Pressure swing adsorption (12%), cryogenic separation (1%) and physical washing (1%) complete the market share (with the exception of 7% of European biomethane plants, with no data available in the EBA database (EBA 2021). For instances, Baker and co-workers (2002) estimated the market share of membrane gas separation technology in 2020 would be five times higher than that of year 2000 (Baker, 2002). Indeed, the market share of MS for biogas upgrading application has increased from 10% in 2012 to 25% in 2017 (EBA 2018). Likewise, MS has grown exponentially since the first industrial application of Prism membranes by Permea (Monsanto) for hydrogen separation from the purge gas stream of ammonia plants (Ismail et al., 2015).
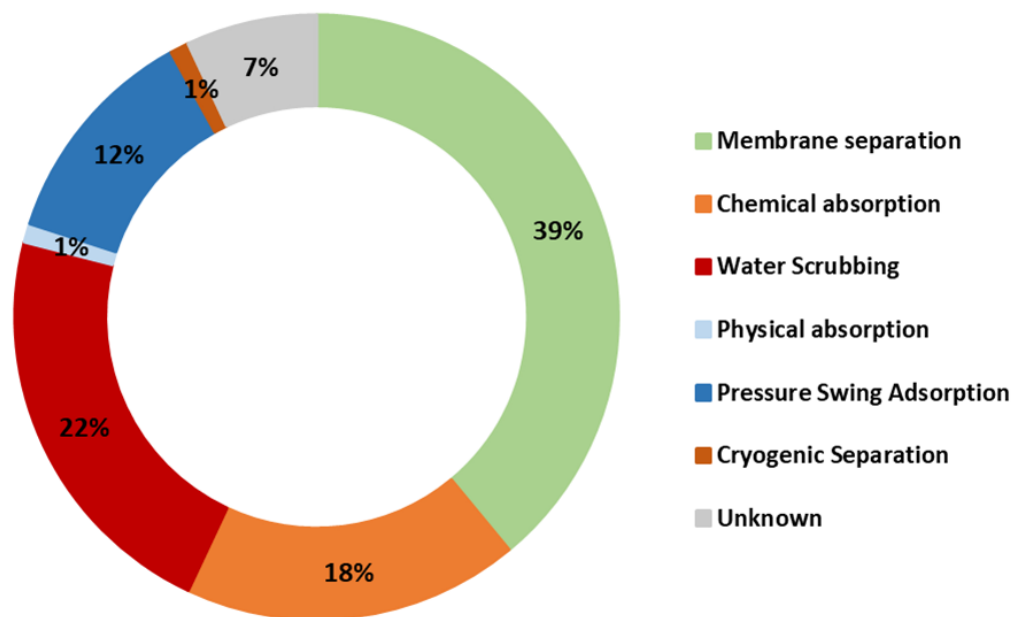
Figure 2. Market share of different upgrading technologies in Europe in 2020 (EBA 2021). Figure adapted from (EBA 2021, 2021)

Ideally, membrane materials for gas separation should exhibit a high selectivity and big fluxes, good mechanical, chemical and thermal stability, a defect-free production and be cost effective. Membranes are classified according to the type of material, configuration, structure, composition, support material and industrial reactions, among others (Figure 3) (Vinoba et al., 2017). Four types of membranes have been proposed for development and commercialization in hydrogen purification: *i*) polymeric membranes (organic), *ii*) porous membranes (ceramic, carbon, metal) *iii*) dense metal membranes and iv) ion conductive membranes, the last three also referred to as inorganic membranes (Adhikari and Fernando, 2006). In this context, dense-metal and polymeric membranes have experienced the largest advances in terms of scale-up (Edlund, 2009). The most commonly used polymeric membranes for gas separation are nonporous membranes, which are classified as glassy or rubbery. Of them, glassy polymers are most commonly applied to gas separation, including polyimides (PI), polysulfones (PSF) and polycarbonates (PC), and are often applied to the separation of O_2/N_2, H_2/N_2, and H_2/CH_4 (Jeon and Lee, 2015). On the other hand, membranes can be configured as flat sheets, hollow fibers, capillaries, and tubular ones and must be installed in a suitable membrane module. The most commonly used modules are pleated cartridges, tubular and capillary, plate-and-frame and spiral-wound, and hollow-fiber modules (Strathmann, 2001).

Hydrogen separation was one of the first applications in gas separations membranes, being DuPont (E. I. du Pont de Nemours and Co, Delaware, USA) the pioneer in manufacturing small-diameter hollow-fiber membranes. Due to the low productivity (or permeance) of these membranes and their high cost, Monsanto Co. (Monsanto Company, Missouri, USA) developed polysulfone hollow-fiber membranes, which considerably increased the transport through the fibers, and consequently were successfully implemented at industrial-scale for hydrogen recovery from ammonia purge gases (Perry et al., 2006). Then, Separex Corp (Champigneulles, France) developed Separex® spiral-wound cellulose acetate membranes (including separations for natural gas and dehydratation (Perry et al., 2006) providing better performance than hollow fiber membranes due to their high resistance of hydrogen impurities (Kaboorani et al., 2012). Polymeric membranes, especially polyimides, have been applied to separate hydrogen from gaseous mixtures (N_2, CO and hydrocarbons) based on their economic viability, easy processability and satisfactory thermal stability (350-450 °C) (Freeman and Pinnau, 2021). Polyimide membranes with excellent heat resistances were introduced by Ube in Japan (Ube Industries, Ltd., Japan), and the refinery at Seibu Oil's (Seibu Oil Company Limited, Onoba, Japan) was the first facility to apply them commercially (Perry et al., 2006). Commercial membrane systems provide a H_2 purity of 90-95% during hydrogen purification with a moderate recovery of 85-90% (Peramanu et al., 1999).
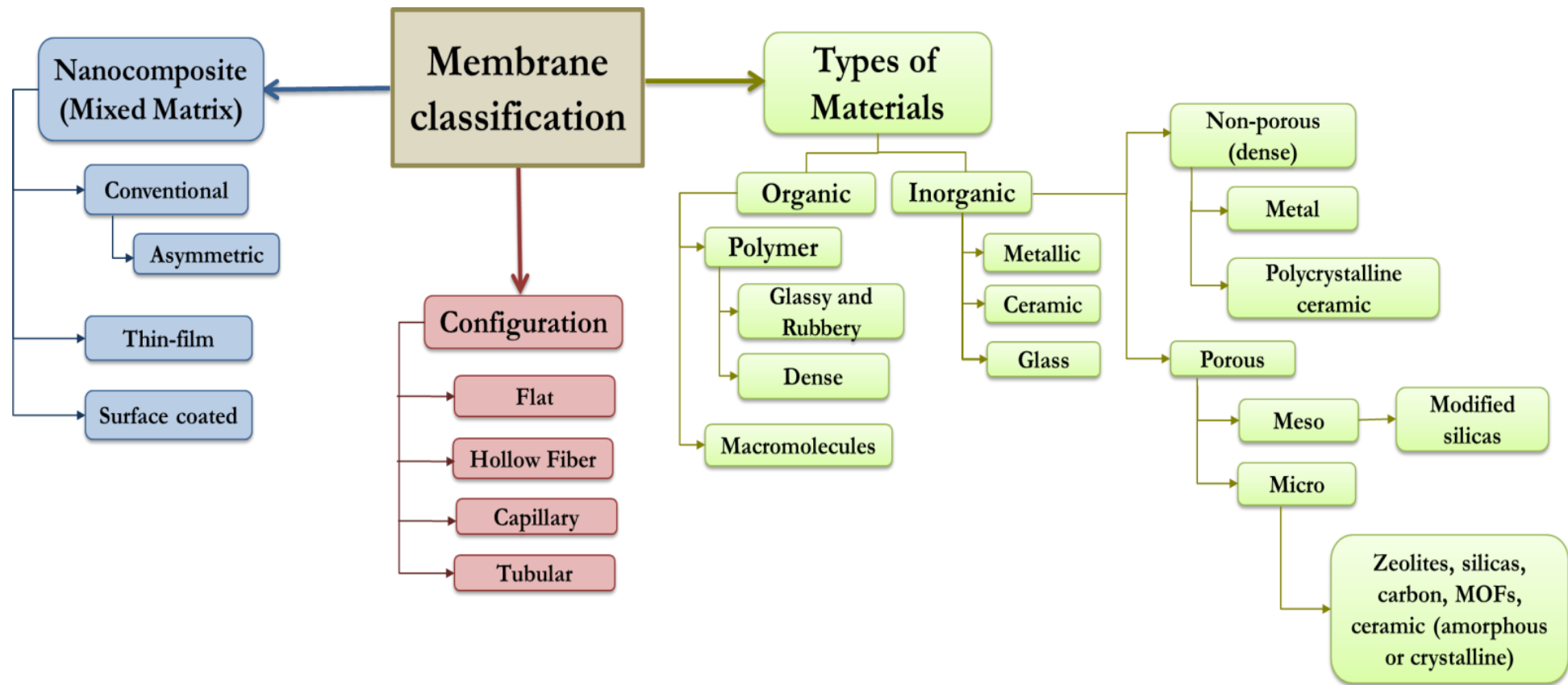
Figure 3. Classification of membranes for gas separation (Al-Mufachi et al., 2015)(Sazali et al., 2020). Adapted from (Vinoba et al., 2017)

In the beginning of the 1990s, gas separation membranes with a poor recovery of methane and low selective were installed for the upgrading of landfill biogas (Petersson and Wellinger, 2009). In 2007, Air Liquide Medal™ further developed and tested new selective membranes able to combine a high methane recovery with a high methane concentration.

Today, membrane-based biogas upgrading can provide methane concentrations of 97-98% in the biomethane with a concomitant methane recovery above 98%, based on the high permeabilities of CO_2 in commercial membrane materials. The permeation rate mainly depends on the size of the molecules and on the membrane construction material (Baker and Low, 2014). Membrane-based biogas upgrading at commercial scale is carried out at 6-20 bar, which entails an energy consumption of 0.18–0.20 kWh/Nm^3 of raw biogas or 0.14–0.26 kWh/Nm^3 of biomethane (Angelidaki et al., 2018).

In this context, despite polymeric membranes have consistently demonstrated promising results and are commercially available at large-scale for hydrogen and biogas purification, their use is limited to 8-9 polymeric materials (e.g., cellulose acetate, polyimides, perfluoropolymer etc.) (Basu et al., 2010)(Ozturk and Demirciyeva, 2013). Therefore, further research in the field of material science needs to be conducted to achieve new membranes with superior gas separation properties: higher permeability, selectivity and stability (mainly restricted plasticization) (Basu et al., 2010).

1.4. Fundamentals of membrane-based gas transport

The membrane gas separation process involves the separation of gases by selective permeation of one or more gaseous components through a thin membrane (porous or dense membrane) (Kohl and Nielsen, 1997). The separation potential of the membrane is determined by its transport properties of the components of a mixture. This transport rate is in turn determined by the permeability and selectivity of the membrane and its driving force (Strathmann, 2001).

Gas separation takes place according to the morphology of the membrane materials and can be based on three transport mechanisms depending on the porous size: Knudsen-diffusion, molecular sieve, and solution-diffusion (Figure 4). In this context, the transport of gases by Knudsen diffusion takes place in porous membranes (pore diameter in the range of 50-100 Å), with smaller pore size than the gas molecules. In this mechanism, gas molecules interact more frequently with the pore walls, colliding with each other, allowing diffusion of lighter molecules to occur through the pores. The molecular sieving mechanism, with pore size between 3.0-5.2 Å, is based on the size exclusion of gas molecules, leading to the

separation of gas molecules of different kinetic size. Indeed, the pores only allow the passage of molecules smaller than that size, preventing the passage of larger ones (Sridhar et al., 2014) (Ismail et al., 2015).
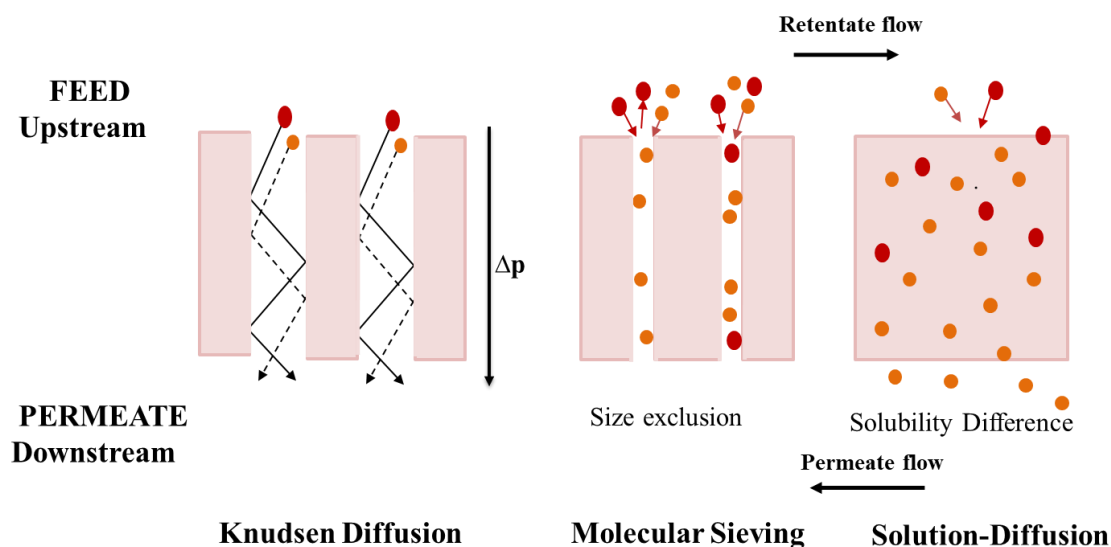

Figure 4. Schematic representation of the three mechanisms for gas separation in membranes: diffusion—Knudsen diffusion, molecular sieving, and solution-diffusion. The figure was adapted from Sridhar and co-workers and Ismail and co-workers (Sridhar et al., 2014) (Ismail et al., 2015).

Gas transport in non-porous dense polymeric membranes is most commonly described by solution-diffusion mechanisms (used exclusively in current commercial devices), which allows gases to pass through the membrane free volume units and consists of three steps (Koros and Fleming, 1993): *i*) sorption in upstream side; *ii*) diffusion through the membrane and *iii*) desorption at the downstream side. Figure 5, shows an schematic overview of mass transfer by solution-diffusion, where gas molecules sorb into the high pressure side of the membrane, then diffuse through along the membrane and later desorb from the low pressure side of the membrane (Wu et al., 2019). This solution-diffusion mechanism is governed by a difference in the thermodynamic activities existing at the upstream and downstream sides of the membrane, as well as the interacting force working between the molecules, which depends on the membrane material and the permeate molecules (Yampolskii, 2012).
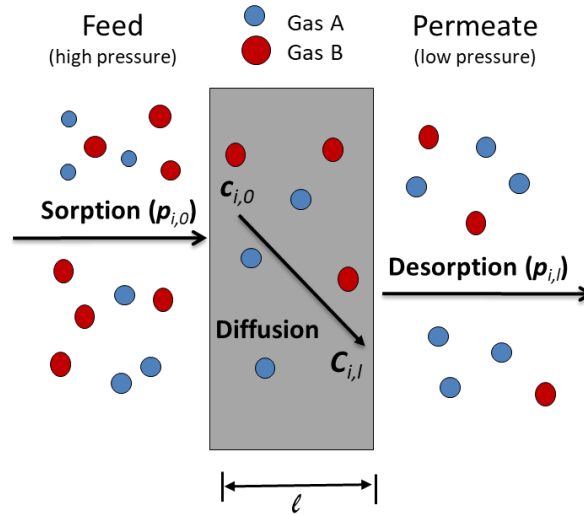
Figure 5. Detailed overview of mass transfer by solution-diffusion model

A key parameter to evaluate membrane transport properties is the Permeability coefficient (P), which refers to the flux of gas through a membrane and is normalized by the thickness and pressure gradient ($p_{i,0}$-$p_{i,l}$) across the membrane (Eq. 1).

$$P = \frac{N_i \, l}{\Delta p} \qquad \text{(Eq. 1)}$$

where N_i is molar flux of a gas component i through the membrane, l is the membrane thickness and Δp is the pressure gradient, calculates as the difference between $p_{i,0}$ (the upstream pressure) and $p_{i,l}$ (the downstream pressure) (Sanders et al., 2013).

The Permeability coefficient ranges from 10^{-4} to 10^4 Barrer as a function of the gas component and the polymer structure (Yampolskii, 2012). Permeability coefficients are expressed in mol (m^2 · s · Pa) in the international system of units. However, P is typically expressed in Barrer, where $1 \, Barrer = 10^{-10} \frac{cm^3(STP).cm}{cm^2 .s.cmHg}$.

The solution-diffusion model also assumes that the equilibrium conditions between sorption and desorption are maintained. In this context, a solubility coefficient, S_i, is introduced, which is the ratio of the concentration of gas dissolved in the polymer, C_i, and the pressure of the gas, p_i, in contact with the polymer (Eq. 2). The solubility of a gas component i in the polymeric material depends mainly on the gas molecule condensability.

$$S_i = \frac{C_{i,0}}{p_{i,0}} = \frac{C_{i,l}}{p_{i,l}} \qquad \text{(Eq. 2)}$$

where $C_{i,0}$ and $C_{i,l}$ represent the concentration of the gas component i at the feed and permeate side, respectively.

On the other hand, the molar flux, N_i, can be expressed as a function of the diffusivity coefficient (D_i) described by the Fick's Law (Eq. 3):

$$N_i = D_i S_i \frac{p_{i,0} - p_{i,l}}{l} \qquad \text{(Eq. 3)}$$

According to the solution-diffusion model, the ability of a gas molecule to pass through the membrane depends on a kinetic factor, the diffusivity, (D_i), which characterizes the movement of the gas molecules diffusing through the polymer, and a thermodynamic factor, the solubility, (S_i), which characterizes the number of gas molecules passing through the membrane. Thus, P can be represented as the product of the diffusion coefficient, D_i, and gas solubility coefficient, S_i (Eq. 4) (Sanders et al., 2013)(Matteucci et al., 2006).

$$P = D_i S_i \qquad \text{(Eq. 4)}$$

On the other hand, a parameter characteristic of gas separation is the ability of a membrane to separate two gas components (A and B). Typically, selectivity is also treated as a material property of the polymer and is represented by Eq. 4. The parameter α is defined as the permeability ratio of the faster permeable gas (P_A) and the slower permeable gas (P_B), so that $\alpha_{AB} > 1$ (Yampolskii, 2012).

$$\alpha_{AB} = \frac{P_A}{P_B} \qquad \text{(Eq. 5)}$$

Usually pure gas permeabilities are used in Eq. 5 giving the so called ideal selectivity (α). Based on the solution-diffusion model, Eq. 5 can be reworded using Eq. 4 and the selectivity of diffusivity and solubility can be expressed using Eq. 6:

$$\alpha_{AB} = \frac{D_A}{D_B} \frac{S_A}{S_B} = \alpha_{AB}^D \, \alpha_{AB}^S \qquad \text{(Eq. 6)}$$

where D_A/D_B is the ratio of the diffusion coefficients of gas components A and B, while S_A/S_B is the ratio of their solubility coefficients. Membrane selectivity determines the energy needed to support gas separation and directly impacts on the operating cost of a membrane system (Galizia et al., 2017).

1.5. Challenges in polymer membranes for gas separation

The transport properties of membranes are determined by factors such as the change in feed composition and the degree of swelling at the gas membrane interface. In addition,

other phenomena such as plasticization and ageing influence the transport properties of membranes. In this context, high concentrations of condensable gases such as CO_2 may plasticize the membrane material. Nowadays, research in membrane-based gas separation targets the development of new membranes with increasing permeabilities and selectivities; specifically, with increasing permeabilities without compromising the selectivity or enhancing the selectivity at constant permeability. Indeed, the increase in permeability without compromising selectivity has been recognized as one of the main target routes to expand the market for gas membrane materials (Adewole et al., 2013).

1.5.1. Trade-Off relationship

Membrane gas separation has been used for the purification of hydrogen (in H_2/CO_2, H_2/CH_4 and H_2/N_2 gas mixtures) in refineries and the petrochemical industry, for the separation of CO_2/CH_4 mixtures (in natural gas sweetening and biogas upgrading) and for the treatment of flue gas (CO_2/N_2) (Baker and Lokhandwala, 2008)(Bernardo et al., 2009)(Brunetti et al., 2010)(Bernardo and Drioli, 2010)(Ockwig and Nenoff, 2007).

As above stated, permeability and selectivity represent key parameters for optimal gas separation. However, these parameters typically experience a trade-off relationship since highly permeable polymers tend to have less selectivity and vice versa. In this context, an experimental upper-bound relationship between selectivity and permeability was proposed by Robeson in order to benchmark membranes for gas separation (Robeson, 1991) (Robeson, 2008). This upper-bound has been used to correlate gas permeability data in a different format. Later on Robeson 1991, Freeman provided a fundamental theory for this observation (Freeman, 1999). As more data on the gas separation characteristics of the polymers used in the 1991 analysis became available, a revised compilation was published in 2008 (Robeson, 2008), where the most significant changes were due to data on perfluorinated polymers that did not exist in 1991. These data show that when the permeability of a gas increases, the permeability of other gases also increases, since the diffusion coefficient of gases is related to the free volume of the polymer (Sanders et al., 2013). Figure 6, displays an example of a Robeson-type trade-off plot for CO_2/CH_4, where the CO_2/CH_4 selectivity is plotted against the CO_2 permeable support material.

Swaidan reported in 2015 new permeability/selectivity "upper bounds" for large-scale commercial membrane-based air and hydrogen separation (Swaidan et al., 2015b). The Robeson upper bound behavior was redefined by Comesaña-Gandara et al. in 2019 for CO_2/CH_4 and CO_2/N_2 separations using ultra-permeable Polymers of Intrinsic Microporosity (PIM)(Comesaña-Gándara et al., 2019).
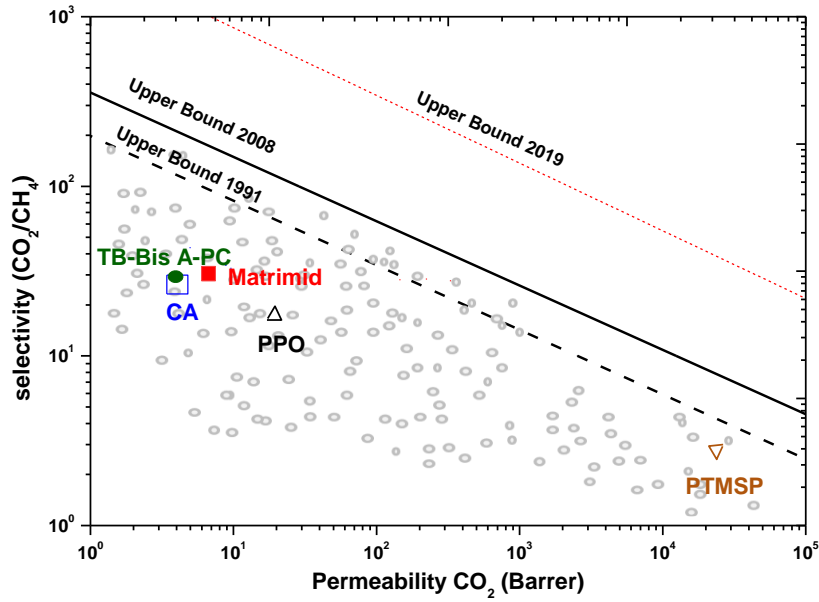
Figure 6. CO_2/CH_4 Robeson diagram for conventional glassy polymers. PTMST: Poly(trimethylsilylpropyne); PPO: poly(phenylene oxide); CA: cellulose acetate; TB-Bis A-PC: tetrabromobisphenol A poly(carbonate); Matrimid®: commercial Poliimide. Pure gas permeabilities were measured between 25 and 35 °C and pressures ranging from 1 to 20 bar. The continuous line represents the 2008 upper bound, and dashed line represents the 1991 upper bound (data taken from (Galizia et al., 2017)).

By transferring this trade-off relationship to the Robeson upper bound, the optimum balance involving a high selectivity in combination with a high permeability is determined. Nowadays, the research in this field is focused on developing new polymer materials capable of exceeding the upper bounds for the most relevant gas pairs. The key variables of the upper bound curves from the upper bound relationships $P_i = k\alpha_{ij}^n$ are tabulated in Table 1, for the present upper bound data versus the prior upper bound data.

Table 1. Tabulation of the values of the front factor k and the upper bound slope n (Robeson, 2008)

Gas pair	k (Barrer)	n
Prior upper bound data (Robeson, 1991)(Robeson et al., 1994)		
O_2/N_2	389,224	-5.800
CO_2/CH_4	1,073,700	-2.6264
H_2/N_2	52,918	-1.5275
H_2/CH_4	18,500	-1.2112
He/N_2	12,500	-1.0242
He/CH_4	5,002	-0.7857
He/H_2	960	-4.9535
CO_2/N_2	NA	NA
N_2/CH_4	NA	NA
H_2/CO_2	1200	-1.9363
He/CO_2	705	-1.220
H_2/O_2	35,760	-2.277
He/O_2	4,600	-1.295
Present upper bound data (Robeson, 2008)		
O_2/N_2	1,396,000	-5.666
CO_2/CH_4	5,369,140	-2.636
H_2/N_2	97,650	-1.4841
H_2/CH_4	27,200	-1.107
He/N_2	19,890	-1.017
He/CH_4	19,800	-0.809
He/H_2	59,910	-4.864
CO_2/N_2	30,967,000	-2.888
N_2/CH_4	2,570	-4.507
H_2/CO_2	4,515	-2.302
He/CO_2	3,760	-1.192
H_2/O_2	NA	NA
He/O_2	NA	NA

1.5.2. Plasticization and Physical Aging

Plasticization is a frequently observed problem affecting the performance of membranes for gas separation (mostly from glassy polymers) (Comesaña-Gandara et al., 2017)(Wind et al., 2002). Plasticization occurs when the gas concentration inside a polymer increases, causing swelling. As a consequence, the free volume and chain movement in the polymer material increase and, in turn, gas diffusion coefficients increase and diffusion selectivity decreases (Paul et al., 1994) (Sanders et al., 2013). A typical phenomenon observed during plasticization of glassy polymers is the increase in the permeability of a pure (or mixed) gas as the partial pressure (upstream) of the gas increases (Wind et al., 2002) caused by the loss of the polymer selectivity. The increase in permeability is driven by the increase in diffusion coefficient, which in turn is governed by the penetrant (upstream) pressure (Singh

et al., 1998). CO_2 is the gas most commonly investigated in plasticization studies (Swaidan et al., 2015a)(Tiwari et al., 2017)(Ying et al., 2019)(Chen et al., 2011). Gas sorption is known to increase after exposing a glassy polymer to CO_2 at a given pressure for a period of time, which can even affect the mechanical properties of the polymer (Chiou and Paul, 1987). For glassy polymers, plasticization typically occurs at pressures of 10-40 bars and CO_2 concentration of 38 $\pm$7 $cm^3(STP)/cm^3_{polymer}$. Since pressure is related to CO_2 concentration in the polymer, it has been hypothesized that each polymer needs the same CO_2 concentration to induce plasticization but a different pressure to achieve it. As a rule of thumb, polymers that absorb more CO_2 are more likely to plasticize than those that absorb less CO_2 at a given pressure (Sanders et al., 2013). The thickness of a glassy polymer film (membrane) represents a key factor in the plasticization process because thinner films tend to be more sensitive to CO_2 pressure changes. Thus, a thin film tends to plasticize more quickly (Horn and Paul, 2011).

There is a wide variety of glassy polymers with outstanding performance in gas separations. These materials, by their nature, are not in equilibrium and have a high free volume due to their inefficient packing (caused by the movement of their chains), which avoids fully equilibrium properties to be reached (Rowe et al., 2009). This gradual approach to equilibrium influences various properties that change over time and consequently the material undergoes "physical aging". This frequent drawback affecting the membrane performance is a gradual continuation of the glass transition that sets in around Tg. Thus, physical ageing affects all temperature-dependent properties that change significantly and sharply at Tg. Ageing can be explained by the concept of free volume (Figure 7). The free-volume concept assumes that the transport mobility of the particles depends mainly on the degree of packing of the system. If packing is efficient, the number and size of free volume elements are reduced, and thus the gas diffuses slower through the membrane over time (Rowe et al., 2009). The rate of physical ageing should then decrease over time because, when the free volume gradually decreases, the driving force governing physical ageing decreases, and also the pace of segmental movements that help reorganize the polymer chains decreases (Sanders et al., 2013).

Physical ageing, apart from reducing gas permeability, also impacts other physical properties with an increase in internal energy accompanied with an increase in entropy (Struik, 1978). Therefore, as the polymer ages, the free volume decreases along with permeability (although at slower rates as time goes on), which is accompanied by an increase

in selectivity as a consequence of the reduction of membrane flux over time (Sanders et al., 2013).
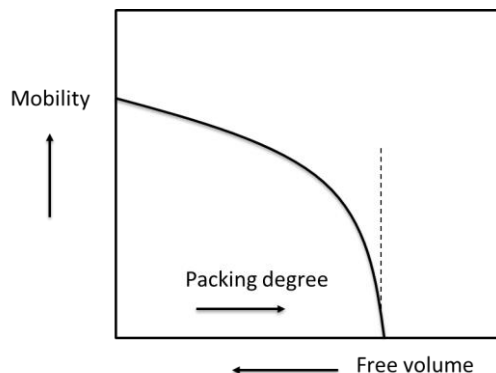
Membrane thickness represents another factor influencing physical ageing. According to Baker and co-workers, the free volume elements migrate to the surface as bubbles, leaving a viscous liquid, with the migration distance being proportional to the square of the membrane thickness. Therefore, rearrangement and loss of permeability occurs in a short time in thin membranes (Baker and Low, 2014). In this context, Tiwari and co-workers investigated the impact of physical ageing on gas permeability in thin and thick membranes manufactured with "high free-volume" glassy polymers (e.g., PIM-1). The results of this study revealed a dominant ageing effect in thin films, where even physical ageing overcame the CO_2 plasticization effects (Tiwari et al., 2017). Figure 8, displays an example of the time course of the decrease in membrane permeability. This effect, using Matrimid® coated with polydimethylsiloxane (PDMS) membranes, was investigated by Rowe and co-workers (2009), who observed that ageing rapidly increases in thinner membranes (Rowe et al., 2009). Likewise, Xia and co-workers (2014), investigated both the effect of the membrane thickness on ageing and the influence of the ageing time on the plasticization using a commercial polyimide membrane, Matrimid®, for gas separation (Xia et al., 2014). This study concluded that membranes become more vulnerable to CO_2 plasticization as their thickness decreases and the ageing time increases (Xia et al., 2014). Finally, it is worth mentioning that the ageing process can be reversed by heating the membrane above Tg (McCaig and Paul, 2000).
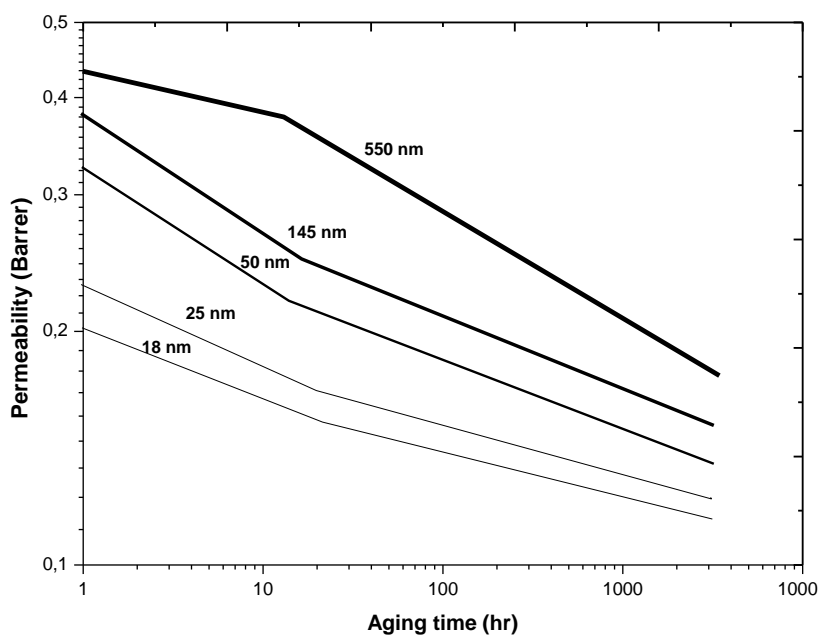
Figure 8. Effect of physical aging films as a function on time and thickness at 35 °C and 2 atm (Adapted from Rowe and co-workers (Adapted from (Rowe et al., 2009)).

1.5.3. Novel polymeric membrane materials for gas separation

Chemical resistance, sorption capacity and good mechanical strength rank among the most relevant criteria for selecting polymeric material for gas separation. However, the intrinsic membrane permeability, the ability of the polymer to resist swelling induced plasticization and the processability of the polymer into a useful asymmetric or thin film composite morphology have been identified as key properties of membrane materials. Moreover, the polymer material should exhibit a good interaction with at least one of the components of the mixture in order to induce an effective separation (Sridhar et al., 2014). Today, research in the field of gas separation is focused on the development of innovative membranes with enhanced permeability and selectivity that exceed the Robeson upper bound limit and, consequently overcome the trade-off effect of conventional membranes (Robeson, 1991)(Robeson, 2008)(Swaidan et al., 2015b)(Comesaña-Gándara et al., 2019).

According to Galizia and co-workers (Galizia et al., 2017), most of the polymers developed for gas separation membranes in the last 30 years were evaluated without systematically proving their superior performance compared to the existing materials. Due to their high flexibility, one of the most synthesized families of materials for creating and understanding structure-property relationships are polyimides (Galizia et al., 2017). However, it has not been possible to significantly improve the structure-property balance of polyimides-based membranes. Therefore, despite polymeric membranes can be used for the separation of almost all gas mixtures, such as O_2/N_2 separation, hydrogen purification

(H_2/N_2, H_2/CH_4, and H_2/CO), CO_2/CH_4 biogas mixtures and vapor/gas separation, it is necessary to move beyond conventional polymers. In this context, new membrane materials for gas separation must provide higher permeabilities and permselectivities than conventional membranes. In addition, the production of new membranes for gas separation must consider good film-forming, good mechanical properties, absence of microdefects in the thin film, excellent chemical and thermal stability as well as absence of ageing (Yampolskii, 2012).

Poly(benzimidazoles) (PBIs) often exhibit glass transition temperatures (Tg) greater than 400 °C, and a good chemical, mechanical and thermal stability, which is uncommon among glassy polymers. Celazole® (PBI Performance Products, Inc., Charlotte, USA) (sometimes referred to as m-PBI in the literature) is an example of membranes derived from PBIs that have been shown to have attractive gas transport properties. However, Celazole® exhibits a low solubility in common solvents due to its structural features and intermolecular hydrogen bonding forces (Vogel and Marvel, 1961)(Borjigin et al., 2015a). Borjigin and co-workers synthesized a novel PBI with sulfonyl moieties by performing a structural modification using 3,3',4,4'-tetraamino-diphenylsulfone (TADPS) as monomer, which entailed a good solubility in common solvents such as N- methyl-2-Pyrrolidinone, NMP, N,N-dimethylacetamide, DMAc and Dimethylsulphoxide, DMSO. Unfortunately, despite the good thermal stability and high permeabilities of PBIs, these materials are still susceptible to physical ageing (Borjigin et al., 2015b).

Aromatic Polyamides (PA) were one of the first aromatic linear polymers considered thermally stable. PA typically exhibit a high cohesive energy density, a strong tendency to show very efficient polymer chain packing and a semicrystalline morphology (Ghosal et al., 1995). Additionally, PA exhibit also a fair balance of properties: high thermal resistance, good mechanical and chemical stability and easier processability than aromatic polyimides (De Abajo et al., 2003). However, PA support a low gas permeability of small molecules compared to polyimides. In recent years, attempts have been made to improve PA gas separation performance by introducing bulky moieties, contoured structures or by introducing hexa-fluoropropane parts into the macromolecular chain, but with a limited success (Espeso et al., 2006) (Maya et al., 2011). Likewise, Lozano and co-workers carried out *in situ* silylation of diamines by adding trimethylchlorosilane (TMSCl) to the diamine solutions that, after the addition of a diacid chloride, resulted in high molecular weight aromatic polyamides, which guarantees high performance (Lozano et al., 1997).

On the other hand, the so-called nanoporous polymers, as a result of their extremely fine nanoporous structure, have shown promising results in terms of gas separation. Examples of these materials are:

i) Polymers of Intrinsic Microporosity (PIMs): PIMs were initially developed by Budd and McKeown (Mc Keown and Budd, 2006) and have been demonstrated to be good candidates for gas separation due to their strong interactions with gas molecules and their nanometer pore size (Budd et al., 2005)(Lanč et al., 2019)(Mc Keown and Budd, 2006). However, their physical ageing and the instability of their permeability properties over time are the major obstacles to their commercialization (Swaidan et al., 2015a)(Baker and Low, 2014)(Tiwari et al., 2017).

ii) Thermally Rearranged polymers (TR): TRs were initially introduced by Park and co-workers in 2007 (Park et al., 2007) and show a high selectivity and an extraordinarily high permeability. Additionally, TRs exhibit a good resistance to plasticization as well as a strong chemical and thermal resistance.

Recently, significant research efforts have been made in the optimization of Mixed Matrix Membranes (MMMs) (Vinoba et al., 2017). MMMs allow tuning the transport properties of conventional polymers for target applications by combining the high permeability of the polymer and the good selectivity of the filler materials.

1.6. Mixed Matrix Membranes

Polymeric membranes have been successful in some gas separation processes such as natural gas sweetening but are still subject to the trade-off between permeability and selectivity, and the impact of physical ageing and plasticization, which makes them unstable for industrial applications. Recently, Barker (2014) reviewed the barriers limiting the development of membranes with high selectivity and permeance -from the last 35 year- and identified the need to develop new materials for new and future membrane applications (Baker and Low, 2014). Therefore, most research efforts are devoted nowadays to the development of new polymeric materials and membranes material such as Zeolites, metal organic frameworks (MOF), carbon molecular sieves, carbon nanotubes and graphenes to improve the gas separation performance of membranes (Dechnik et al., 2017).

In this context, hybrid materials known as MMMs have been manufactured by adding specific, frequently inorganic, materials as the disperse phase into polymers in order to take advantage of the processability of polymers and simultaneously overcome the trade-off between permeability and selectivity. The concept of mixed matrix membranes has been

described in multiple scientific publications. According to the most recent definitions, MMMs results from the combination of an inorganic or organic materials (micro or nanoparticles) -in the form of dispersed particles called additive or filler- and a polymeric matrix -continuous phase- (Dechnik et al., 2017) (Bernardo et al., 2009)(Figure 9). PIMs and HPI are the most commonly used polymeric matrices, and zeolites the most common fillers. Moreover, MMMs have been recently thermally treated to obtain MMM-TR with outstanding gas transport properties for gas pairs such as CO_2/CH_4, O_2/N_2, H_2/CO_2, etc. (Kim et al., 2018a) (Kim et al., 2018b) (Wang et al., 2018) (Smith et al., 2019) (Khdhayyer et al., 2017).
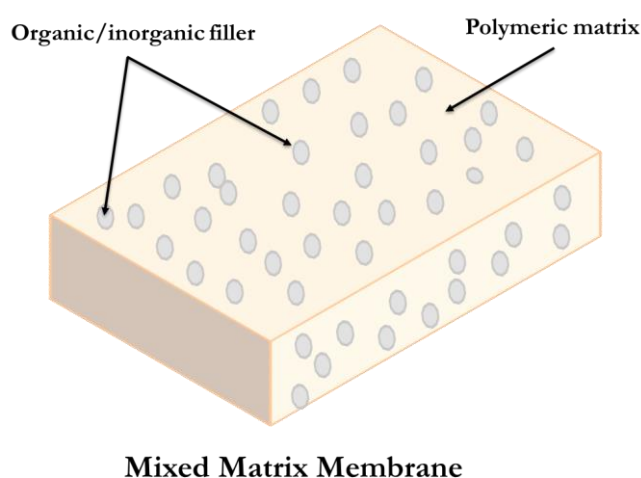

Figure 9. Schematic of a mixed matrix membrane (adapted from (Lin et al., 2018)).

The main objective of the manufacture of MMMs is to provide solutions to the existing permeability versus selectivity trade-off relationship of gas separation polymeric membranes by taking advantage of the superior properties of inorganic particles (Vinh-Thang and Kaliaguine, 2013) (Dong et al., 2013). In addition, MMMs compensate the unavoidable fragility limitation of inorganic membranes using a flexible polymer as the continuous matrix. These features provide MMMs with the potential to achieve a greater selectivity, permeability (caused by increasing the diffusion coefficients) or both, compared to existing polymeric membranes and to exceed the upper limit proposed by Robeson. These inorganic and organic materials used as fillers should have a unique structure, surface chemistry and mechanical strength. Inorganic fillers contribute to enhanced diffusivity selectivity by acting as molecular sieves due to their precise pore size and shape and geometry, thus overcoming the properties of common polymeric membranes (Aroon et al.,

2010)(Galizia et al., 2017). Overall, MMMs support unprecedented increases in permeability while maintaining selectivity by introducing fillers into the polymeric matrix, as a result of the increase in diffusion coefficients.

The first reports of the manufacture of MMMs were published in the 1970s. For instance, Paul and Kemp (1973) added a commercial zeolite (Molecular Sieve Type 5A) as a filler to a PDMS rubber used as polymer matrix (Paul and Kemp, 1973). A good interaction between the polymer and the zeolite was observed due to the flexibility of the rubber polymer and a large increase of a delayed diffusion time lag effect. However, high fluxes of gas in the polymer matrix can result in a low improvement in the selectivity (Bernardo et al., 2009). In the last decade, preparation of MMMs, investigation of their transport and mechanical properties, and the study of their nanostructure have attracted the attention of the membrane community (Yampolskii, 2012).

1.6.1. Factors influencing mixed-matrix membrane manufacture

There are multiple factors that, during the manufacture of MMMs, can induce: interfacial defects caused by particle sedimentation (due to the differences in physical properties and density with the polymer), agglomeration or migration of filler particles to the surface, especially when the load of fillers is high due to the fact that this scenario increases the diffusion distance within the solid phase agglomerate (Vinh-Thang and Kaliaguine, 2013).

According to Noble (2011), the compatibility between the disperse and continuous phases in terms of permeability is an import factor to consider due to the fact that the resistance to mass transfer is typically much higher in phases with much lower gas permeability (Noble, 2011). In addition, there is a relationship between the filler particle size and membrane thickness, as smaller particles provide a higher surface area/volume ratio, which supports a greater mass transfer between phases. Finally, an effective contact between the two phases is necessary to avoid any gaps between them that could block the access to the pores (Noble, 2011).

Today, the achievement of the desired morphology, gas separation properties and mechanical/chemical stability in MMMs requires overcoming multiple manufacturing challenges such as: obtaining a flawless interface to guarantee a good separation performance of the membranes, obtaining an homogeneous dispersion between the two phases, avoiding agglomerations responsible for low selectivity and finally selecting materials with excellent separation properties and good compatibility between the phases (Aroon et al., 2010) (Chung et al., 2007).

1.6.1.1. Morphologies of the mixed-matrix membrane

The ideal morphology of MMMs involves no defects in the polymer–particle interface and must guarantee gas transport through the dispersed phase instead through the continuous phase (polymeric matrix) (Figure 10) (Dong et al., 2013). This ideal morphology is based on the ideal Maxwell model and represents an idealized case for mixed matrix transport properties (Moore and Koros, 2005). This model, described by Robeson as a dilute suspension of particles in a polymeric matrix, was mainly developed for estimating dielectric properties of composites and describes the effective permeability of MMMs, P_{eff}, as follows (Tena et al., 2014) (Zimmerman et al., 1997):

$$P_{eff} = P_c \left[\frac{P_d + 2P_c - 2\phi_d (P_c - P_d)}{P_d + 2P_c + \phi_d (P_c - P_d)} \right] \qquad \text{(Eq. 7)}$$

where P_c is the permeability of the continuous phase (i.e., polymer matrix), P_d represents the permeability of the dispersed phase (i.e., filler) and Φ_d is the volume fraction of the dispersed phase. Note that Eq. 7 goes to the appropriate value of P in the limits as $\phi_d = 0$ or 1. Maxwell's model can be complicated by assuming that the dispersed phase, being uniformly distributed, is encapsulated by an "interface" (region between inorganic fillers and polymer matrix) with properties different from both the dispersed and continuous phases (Moore and Koros, 2005) (Noble, 2011). The formation of the interface is attributed to the inhibition of the mobility of the polymer chains in compressive stress near the polymer-particle interface. Figure 11, shows a representation of the polymer matrix, the dispersed phase and the rigidified interface (three-phase MMM system) (Shimekit et al., 2011).
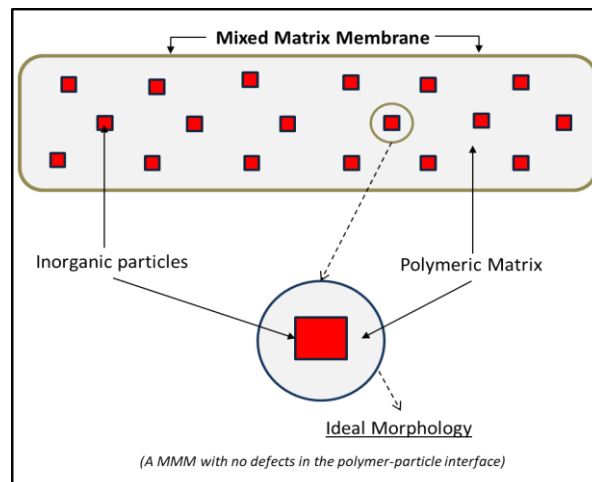
Figure 10. Schematic diagram of an ideal MMM.

One of the disadvantages of this model for MMMs is the need to determine the transport properties (e.g., through kinetic sorption in monodispersed crystals) in order to obtain a good characterization of the dispersed phase (Moore and Koros, 2005). Moreover, it is also only applicable to low filler loadings with free volume fractions lower than 0.2. In this context, high values of Φ_d render the ideal Maxwell model useless. In addition, the Maxwell model does not consider the morphological properties of the filler such as particle shape particle size distribution or the aggregation of filler particles (Vinh-Thang and Kaliaguine, 2013).

In fact, the manufacture of an ideal MMM is a complex process due to the formation of defects at the polymer-particle interface that may arise due to a weak polymer-particle adhesion, caused by the difference in properties between both phases (Aroon et al., 2010). These defects at the interface between dispersed and continuous phases can affect membrane properties, mainly the separation performance of the membrane.
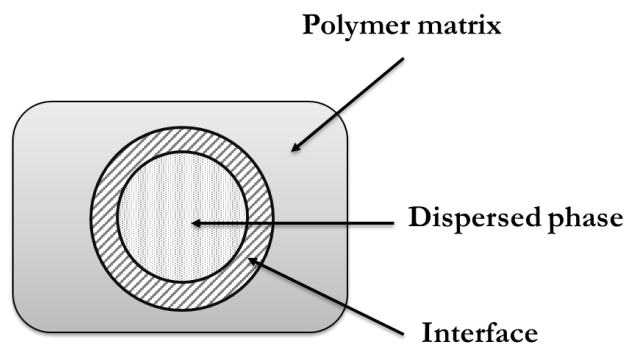
Polymer matrix

Dispersed phase

Interface

Figure 11. Schematic representation of polymer matrix, dispersed phase, and their interphase

The most common factors responsible of interfacial defects can be classified into three major categories: i) Interfacial voids or sieves- in-a-cage, ii) Rigidified polymer layer around the inorganic fillers, and iii) Particle pore blockage (Vinh-Thang and Kaliaguine, 2013) (Moore and Koros, 2005)(Chung et al., 2007).
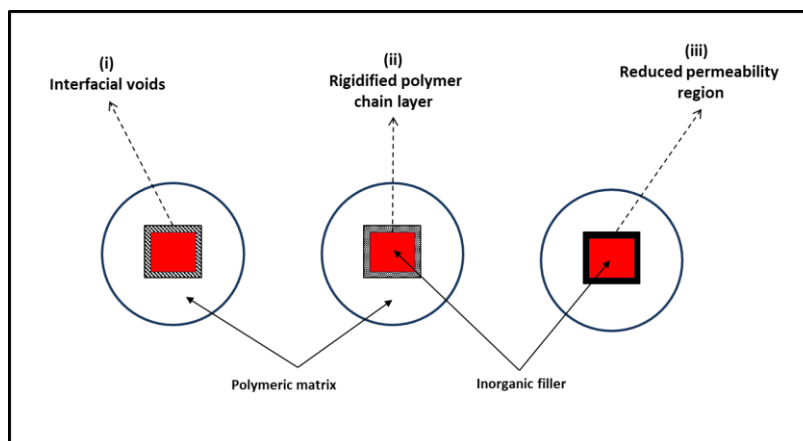
Figure 12. Schematic diagram of an interface void (i), rigidified polymer (ii) and partial blockage (iii) in MMMs. (Adapted from (Aroon et al., 2010))

A low adhesion between the dispersed phase and the continuous phase could lead to the formation of non-selective voids in the interfacial region (Figure 12, case i). Other causes contributing to the formation of interfacial voids are the alteration of the polymer packing in the vicinity of the dispersed particles, the repulsive force between the two phases, the different coefficients of thermal expansion and the elongation stress during fiber spinning (Vinh-Thang and Kaliaguine, 2013). Moreover, interfacial voids or sieves- in-a-cage are attributed to the de-wetting of the polymeric chains on the external surface of the particles (Dong et al., 2013). Moore and Koros (2005) observed that solvent evaporation, thermal effects and the resulting stresses at the polymer-disperse phase interface cause defects such as interface void formation, due to the partial or apparent clogging of the dispersed phase (Moore and Koros, 2005). The formation of these defects allows the gases to pass and, hence, deteriorates the apparent selectivity and increases the permeability of MMMs.

Rigidified polymer layer around the inorganic fillers occurs when the polymer matrix chains, in direct contact with the filler surface, are rigidified as compared with the bulk polymer chains, which reduces the free volume and is related to a uniform tension around the particles (Chung et al., 2007)(Aroon et al., 2010). Moore and Koros (2005) hypothesized that polymer rigidification (Figure 12, case ii) enhanced the diffusive selectivity and decreased membrane permeability (Moore and Koros, 2005).

Particle pore blockage occurs when the surface pores of the filler are partially blocked by the rigidified polymer chains (Figure 12, case iii). This clogging is usually generated by the presence of sorbent, solvent traces, a contaminant or a minor component in the feed gas, before, during and after the manufacture of the MMMs (Zimmerman et al., 1997)(Chung et al., 2007)(Moore and Koros, 2005)(Mahajan and Koros, 2000). However, there is no accurate

methodology to differentiate the influence of these factors. Based on previous research, if the pores are completely blocked, the gas cannot pass through the particle fillers, and no enhancement in selectivity over the neat polymer is reached as in the case of MMMs filled with nonporous particles.

The formation of rigidified polymer layer around the inorganic fillers and particle pore blockage are caused by sorption of a strongly retained molecule. In the first case, the strongly retained molecule completely prevents the penetrants of interest from entering the dispersed phase, while in the second case, the penetrants of interest enter or pass through the dispersed phase more slowly than usual (Moore and Koros, 2005)(Chung et al., 2007).

In summary, poor adhesion, mobility of polymer matrix chains and pore clogging by the matrix are just some of the phenomena observed when incorporating a dispersed phase into a continuous phase during the fabrication of MMMs.

Methods for manufacturing defects-free membranes

Poor adhesion and repulsive forces between the continuous and disperse phases, incompatibility between polymer and filler, solvent evaporation during membrane formation, polymer packing disruption in the vicinity of the inorganic phase, and different thermal expansion coefficients for polymer and filler can induce multiple interfacial defects and non-ideal morphologies in MMMs (Aroon et al., 2010). In order to avoid these interfacial defects and manufacturing defect-free MMMs, the following methodological strategies have been applied:

An important factor during the manufacture of an ideal MMM with optimal performance is the homogeneous distribution (or dispersion) of the filler within the continuous phase in order to guarantee an effective filler/polymer contact (Dong et al., 2013). In fact, a poor filler distribution can affect membrane performance by agglomeration, which leads to the formation of non-selective interfacial voids (Lin et al., 2018). Unfortunately, high filler loadings can sometimes result in particle aggregation, which can form voids within the particle aggregates that cannot be reached by polymer chain segments and act as channels facilitating gas molecules transport, thus reducing the selectivity of the MMMs. Similarly, high filler loadings can cause sedimentation, which also contributes to the poor dispersion of the filler into the continuous phase (Dong et al., 2013). This filler agglomeration entails the creation of pinholes that cannot be reached by polymer segments, resulting in non-selective defects in MMMs (Chung et al., 2007).

In this context, the so called "priming" method created by Mahajan and Koros (2002) is the most common strategy to avoid filler agglomeration (Mahajan and Koros, 2000). This technique can reduce the stress at the filler/polymer interface, thus resulting in an improved interaction between the polymer primed filler and the bulk polymer, concomitantly with a reduced agglomeration of the filler(Aroon et al., 2010)(Dong et al., 2013). This prime method consists in dispersing the particles in a suitable solvent, subjecting them to sonication followed by coating the surface of the filler in suspension. This coating is carried out by adding a small percentage of homogeneous polymer solution prior to the dispersion in the bulk polymer solution (Mahajan and Koros, 2000). On the other hand, the preparation of polymer diluted solutions to increase the viscosity and decrease membrane thickness have been proposed to avoid agglomeration since this methodology can reduce particle sedimentation. Alternatively, the membrane can be cast " quickly " so that the fillers do not have time to precipitate.

Finally, another approach to achieve flexibility during membrane formation is to mimic the use of a low Tg polymer by forming the membrane close to the Tg of the polymer matrix used as precursor of the MMMs. An obvious limitation of this strategy is the common tendency to use suitable casting solvents that boil at temperatures below the Tg of a typical rigid polymer like Matrimid (Mahajan et al., 2002).

1.6.1.2. Polymer materials

The optimum selection of materials for both the continuous phase and the dispersed phase is a key factor during the development of MMMs since the properties of the precursor materials can affect the morphology and separation performance of membranes (Chung et al., 2007). Despite the selection of optimum fillers was the major concern in the early manufacture of MMMs, the selection of the polymer used as the matrix greatly impacts the gas separation performance of MMMs (Chung et al., 2007).

In the field of gas separation using membranes, rubbery and glassy polymers have been traditionally used. Rubbery polymers contain flexible polymer chain structures and have the ability to stretch the chains apart, the chains returning to their original position when tension is released. Rubbery polymers also exhibit a high permeability and a low selectivity for the separation of common gas pairs, as a result of the different condensability of the gas components (Bernardo et al., 2009). On the contrary, glassy polymers possess rigid chain structures with restricted segmental motion. This rigid chain structure offers desirable separation properties such a high selectivity combined with medium/low permeability (Ismail et al., 2015). The high selectivity of glassy polymers can be attributed to their lower

free volume, the narrower distribution of the free volume and the lower flexibility of the polymer chains compared to their rubbery counterparts.

Due to the high degree of mobility, rubbery polymers ensure good adhesion between the polymeric matrix and the fillers, which can avoid interfacial voids and facilitate the manufacture of defect-free MMMs. However, a high mobility also entails a high permeability, which suggests that gas transport is dominated mainly by the polymer matrix and only a small portion is attributed to the filler. On another hand, although glassy polymers exhibit superior properties than rubbery polymers, their rigid chain structure typically results in a poor adhesion of the pair polymer-filler, thus generating voids at the interface (Dong et al., 2013). Therefore, the gas transport properties of the materials and adhesion between the phases should be carefully considered when selecting the polymer matrix (Aroon et al., 2010). In this context, novel polymers capable of separating gas mixtures by solubility selectivity are needed.

Material selection to manufacture MMMs is a complex task, especially for glassy polymers. However, a considerable number of glassy polymers are being employed as continuous phase in MMMs such as cellulose acetate (CA), polysulfone (PSU), polyimide (PI), polyamide (PA), polyethersulfone (PES), polypropylene (PP), poly-vinylidene fluoride (PVDF) and perfluorinated materials, etc. (Nasir et al., 2013) (Aguilar-Lugo et al., 2019) (Kim et al., 2018b) (Smith et al., 2019). Polymers such as PMP (4-methyl-2-pentyne), PTBA (tert-butylacetylene) and PTMSP (1-trimethylsilyl-1-propyne), namely "reverse-selective polymers", have been also used as continuous phase due to their high fractional free volume. In the latter membranes, the gas transport mechanism shifts from being controlled by diffusivity to being controlled by solubility (contrarily to the observations in traditional low-free volume glassy polymers), and therefore, transport properties are favored for more condensable species (e.g., CO_2) than for smaller molecules (Merkel et al., 2003).

In recent years, the most common materials developed for the manufacture of MMMs are divided into three groups: (i) Advanced high permeability polymers (PIM, Polyimides and TR polymers), (ii) Polymers with moderate permeability and high selectivity and (iii) Ionic liquid/poly ionic liquids with high permeability and high selectivity (Ebadi Amooghin et al., 2019). For instance, a limited number of researchers have studied the transport properties using PIM-1 as a continuous phase for the separation of CO_2/CH_4 with a notable increase in permeabilities compared to the matrix. These studies also demonstrated that the introduction of a filler (ZIF-8) to this polymeric matrix mediates an increase in free volume, as a result of the combination of the contributing cavities and looser polymeric

chains at the boundary between the filler and the PIM-1 matrix (Khdhayyer et al., 2017) (Bushell et al., 2013) (Tien-Binh et al., 2016). These membranes represent good candidates for CO_2 removal from biogas, although they suffer from severe physical ageing. On the one hand, the introduction of TR materials (e.g., hydroxypolyimide, HPI, and hydroxypolyamide, HPA) as a continuous phase has been proposed as a promising alternative since TR polymers show superior gas separation properties and can help to reduce non-selective voids during the manufacture MMMs (Kim et al., 2019) (Smith et al., 2019)(Aguilar-Lugo et al., 2021).

The permeation properties of MMMs are mainly determined by the shape and size of the filler, its pore size, pore size distribution, sedimentation and agglomeration properties and the gas separation operational conditions (gas composition, pressure, and temperature). In addition, the permeability of both the continuous and disperse phase should be comparable since a continuous phase with a high permeability reduces the contribution of the filler to gas separation (Vinh-Thang and Kaliaguine, 2013).

1.6.1.3. Advanced functional fillers

The major challenges encountered during the manufacture of MMMs are the selection of adequate fillers that provide a good interaction with the polymer for the enhancement of gas separation properties. Indeed, the addition of suitable fillers in the polymer matrix results in a significant increase in the overall separation efficiency and therefore in a superior gas selectivity performance by MMMs (Vinoba et al., 2017).

There is a great variety of fillers that have been used in the development of MMMs as disperse phase. In recent years, the synthesis of novel organic/inorganic membrane materials has yielded in emerging materials used as high-performance fillers in MMMs for gas separation. Here, the most studied fillers (with a good compatibility with polymers) to date are briefly reviewed, particularly Zeolites, Metal Organic frameworks (MOFs), Covalent Organic Frameworks (COFs), Porous Aromatic Framework (PAFs) and Porous Polymer Networks (PPNs), recently named Porous Organic Polymers (POPs) (Esteban et al., 2020), the latter used for the development of our research (Figure 13).
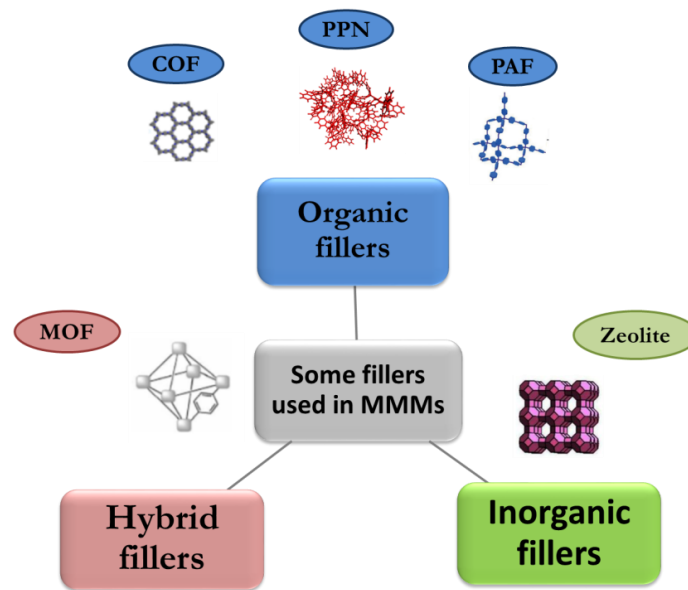
Figure 13. Some types of fillers used in MMM preparation (Adapted from (Ebadi Amooghin et al., 2019).

Zeolites

Based on structural features, zeolites are an inorganic material frequently used as disperse phase for the manufacture of MMMs. Zeolites are hydrated aluminosilicate materials with opened three-dimensional framework structures that possess regular intracrystalline cavities and channels of molecular dimension (3-12 Å). Therefore, zeolites are materials with shape/size-selective nanopores (Kim et al., 2012)(Goh et al., 2011). One of the most relevant properties of this filler is sorption and diffusion due to the different sizes of its channels and cavities, which determines the free space or void volume of the MMMs (Goh et al., 2011). Zeolites possess interesting thermal and chemical stability, a well-defined microstructure and high mechanical strength, which makes them suitable candidates to be used as a dispersed phase in the manufacture of MMMs(Sanaeepur and Kargari, 2015)(Bastani et al., 2013). Interestingly, the low packing density of zeolites makes them an unsuitable material for gas separation, however their use as a dispersed phase in the fabrication of MMMs provides an opportunity to overcome this problem (Dong et al., 2013). In addition, zeolites exhibit a permeability and selectivity superior to polymeric materials due to their unique molecular sieving characteristics.

Zeolites have traditionally received attention as potential fillers due to their thermal stability and promising separation and transport properties. Thus, the specific sorption properties and shape selectivity of zeolites, when applied to polymers with easy processability, provide superior gas separation properties to MMMs (Goh et al., 2011). Several investigations have shown that the transport properties of MMMs are affected by the

type of zeolite used. For instance, MMMs prepared with zeolite 4A support an effective O_2/N_2 separation due to their adequate pore size (3.8-4.0 Å), with selectivities up to 37. Membranes with zeolite 5A as filler exhibit much higher H_2/N_2 and O_2/N_2 selectivity than membranes with zeolite 4A as filler. In this context, Zeolites are still of interest for membrane investigations despite providing low permeabilities for O_2 (0.8 Barrer) (Mahajan and Koros, 2002) (Muhammad Hussain, 2012).

Despite the promising results obtained in the lab, MMMs with zeolites as the dispersed phase have not been commercially exploited due to the poor adhesion at the zeolite-polymer interface (especially glassy polymers), resulting in a "sieve-in-a-cage" morphology. This defect is responsible for the non-selective penetration of gas molecules, the reduction in selectivity and poor mechanical properties, especially in the formation of thin films. In addition, high zeolite loadings often result in non-uniform dispersions in MMMs (Galizia et al., 2017).

Metal Organic Frameworks

Metal Organic Frameworks, MOFs, are hybrid materials prepared by combining organic ligands with metal ions or metal-oxide clusters. Ligands play a key role defining the final framework of MOFs, while metal ions also influence the structure of MOFs due to their tunable geometries (Kuppler et al., 2009). MOFs are highly porous chemically mutable materials, with unique properties, different pore sizes and shapes, and multiple functional sites and high specific surface areas that allow creating a wide variety of crystals (Dechnik et al., 2017) (Ebadi Amooghin et al., 2019). Compared to zeolites, the tunable structure of MOFs results in fillers that allow carry organic linkers with high affinity to the polymer chains, thus reducing non-selective defects at the polymer-filler interface. The partially organic nature of MOFs supports a better polymer-filler interaction, which represents a structural advantage compared to other porous materials (Galizia et al., 2017).

In order to optimize gas diffusion and selectivity, new strategies for the formation of high-performance MMMs using MOFs as dispersed phase have been assessed. A wide variety of MOFs subfamilies with ultrasmall aperture sizes have been chosen as potential fillers. The most typically studied MOFs are Zeolitic Imidazolate Frameworks (ZIFs), copper-based MOFs (Cu-MOFs), Materials Institute Lavoisier (MIL) series, MOF-74 series, and University of Oslo-66 (UiO-66) series (Cheng et al., 2018). ZIFs possess a similar topology to zeolites with tunable pore structures and with high thermal and chemical stabilities (Vinoba et al., 2017). In this context, ZIF-8, HKUST-1, MIL-53, MIL-101, MOF-74, and UiO-66 have

been specifically tested. For instance, ZIFs-8 are a new class of porous crystals (3.4 Å pore aperture and 11.6 Å cages) (Park et al., 2006) composed of tetrahedral metal ions (typically zinc or cobalt) forming extended three-dimensional structures bridged by imidazolate (Im) (Phan et al., 2009). Recently, Kertik and co-workers (Kertik et al., 2017) created *in-situ* molecular sieves with controlled heat treatment up to 350 °C for 24 h for Matrimid/ZIF-8, obtaining excellent selectivity for CO_2/CH_4 gas mixtures due to the excellent interfacial filler-polymer adhesion. Matrimid®/ZIF-8 (40 wt%) thermally treated MMMs exhibited a CO_2 permeability of ~ 1.9 Barrer and a CO_2/CH_4 selectivity of ~ 134 at 40 bar, 35 °C with gas mixtures containing 50 vol% CO_2/50 vol% CH_4 (Galizia et al., 2017) (Kertik et al., 2017).

Finally, it should be stressed that the preparation of membranes with well-dispersed fillers, good filler-polymer interfacial adhesion and a defect-free membrane surface represents nowadays the major challenges of MOF-based MMMs (Y. Zhang et al., 2016).

Covalent Organic Frameworks

Covalent Organic Frameworks, COFs, developed by Côté and co-workers in 2005 (Coté, et al., 2005) have been recently proposed as a type of porous organic materials used as a filler for the fabrication of MMMs. COFs are crystalline porous materials synthesized by the covalent combination of rigid and stable organic monomers (phenyl diboronic acid and hexahydroxytriphenylene), which offer superior chemical and thermal stability compared with MOFs (Wu et al., 2017)(Díaz and Corma, 2016). Moreover, COF materials have a well-defined and predictable 2D or 3D crystalline structures as a result of the formation of strong covalent bonds (Ding and Wang, 2013). Due to their variable structures, easily modifiable scaffold and high affinity to the polymeric matrix, good thermal stability, appropriate solvent compatibility, COFs have demonstrated to be excellent candidates in the field of gas separation (Ebadi Amooghin et al., 2019)(Gao et al., 2014)(Huang et al., 2015)(Hao et al., 2014). Despite the advantages offered by COFs, a limited research has been conducted with COF-based MMMs. For instance, Wu and co-workers (2017) incorporated COFs as particles into PIM-1 as a polymeric matrix, obtaining a remarkable improvement in CO_2 permeability and CO_2/CH_4 and CO_2/N_2 selectivity compared to pure PIM-1 (Wu et al., 2017). Likewise, Biswal and co-workers (2016) manufactured MMMs incorporating TpBD into polybenzimidazole (PBI), resulting in permeabilities above 18 barrer for CO_2 and selectivities of ~ 48 and 23 for CO_2/CH_4 and CO_2/N_2 respectively (Biswal et al., 2016).

Porous Aromatic Framework, PAFs, are a subfamily of Covalent Organic Frameworks (COFs) that, unlike traditional COFs and MOFs, are more strong and stable and exhibit a good physical-chemical stability (Ebadi Amooghin et al., 2019). PAFs are synthesized via irreversible cross-coupling reactions by aromatic rigid linkers (Díaz and Corma, 2016). Due to their covalent backbone, PAFs are chemically robust materials, although with a high irregular internal structure that reduces their porosity and associated crystallinity (Dechnik et al., 2017) (Díaz and Corma, 2016). Moreover, these fillers exhibit a high porosity, narrow pore-size distributions for amorphous solids and Brunauer−Emmett−Teller (BET) surface areas as high as 5200 $m^2 g^{-1}$, which typically results in high affinities for adsorption of CO_2 and other gases. (Dechnik et al., 2017) (Lau et al., 2014). PAF surface area and CO_2 capture may vary depending on the batch, tetrahedral core, phenyl chain length, functionalization and also the arrangement of the nanoparticles in the fillers (Lau et al., 2015).

However, despite their exceptional surface areas and good thermal and hydrothermal stability, PAFs exhibit weak interaction with gases, which limits their gas storage capacity and operating temperature (Konstas et al., 2012). In this context, Ben and co-workers synthesized a porous aromatic framework PAF-1 via phenyl-phenyl coupling with a Langmuir surface area of 7100 $m^2 g^{-1}$ (Ben et al., 2009). Likewise, Lau and co-workers demonstrated that the addition of PAF-1 as disperse phase into PTSMP and poly(methylpentyne) (PMP) can mitigate the permeability loss associated with physical ageing of these super glazed polymers (Lau et al., 2014).

Porous Polymer Networks

Recent investigations have attributed new merits for gas separation to this family of adsorbents as a result of their high thermal and chemical stability, easy processing and low cost (Lu et al., 2010). PPNs are synthesized by the homocoupling of tetrahedral monomers, exhibit high thermal and chemical stability and are insoluble in conventional solvents. PPNs possess Langmuir surface areas as high as 5323 $m^2 g^{-1}$ (Lu et al., 2010)

A new generation of PPNs, also namely Porous Organic Polymers, POPs, was recently developed by reacting rigid trifunctional aromatic monomers with ketones exhibiting electron-withdrawing groups, in superacidic media via acid-catalyzed condensation (Lewis or Brönsted) at low temperatures. PPNs are microporous materials with Brunauer−Emmett−Teller (BET) surface areas ranging from 580 to 790 $m^2 g^{-1}$, and attractive

properties such as: excellent CO_2 uptake capacity as solid adsorbents (up to 207 mg g^{-1} (105 cm^3(STP) g^{-1}) at 0 °C and 1 bar), ability to regenerate by vacuum without heating and an exceptional chemical and thermal stability (Aguilar-Lugo et al., 2019) (Lopez-Iglesias et al., 2018)(Esteban et al., 2020). Their easy synthesis and high conversion render PPNs as materials easy to scale-up. In addition, these materials present a selective adsorption of CO_2 (32.7) superior to N_2 (22.5) under postcombustion conditions, which are higher when compared to other high-performance microporous materials (Aguilar-Lugo et al., 2019). In this context, Aguilar-Lugo and coworkers added PPNs (in different loads) as filler into Matrimid®, resulting in an improvement in the permeability of up to 700% for the gases tested without significantly affecting selectivity (CO_2/N_2 and CO_2/CH_4 selectivities decreased by 4% and 12%, respectively). These authors also observed a good filler-polymer adhesion, which was supported by the increase in the Tg of the MMMs compared to the pure polymer matrix (Aguilar-Lugo et al., 2019). Likewise, Rico-Martínez and coworkers (2022) added, bipyridine moieties-based on POPs into an aromatic poliimides at differents loads. As a result, obtained 4- and 7-fold increases in CO_2 and CH_4 permeability, respectively (Rico-Martínez et al., 2022)(Rico-Martínez et al., 2022).

1.7 Thermally Rearranged Polymers.

As previously mentioned, new materials with superior gas separation performance, increased selectivity and chemical/thermal resistance to aggressive feed conditions are needed. Significant advances have been generated in the chemistry of polymeric membranes for gas separation, mainly aimed at increasing the molecular stiffness and improving the free volume fraction (FVF) of membranes, leading to a high permeability without a significant decrease in selectivity (Comesaña-Gándara et al., 2014) (Smith et al., 2015). In this context, glassy polymers such as polybenzoxazoles (PBO), polybenzothiazoles (PBT), polypyrrolones (PPL) or benzimidazoles (PBI), represent a class of rigid-rod ordered polymers with outstanding mechanical and thermal properties, and extreme rigidity (Hu et al., 2003). However, these materials are unattractive in gas separation because their efficient packing entails few free volume elements accessible to gas penetration, which hinders their manufacture in the form of flexible and tough films. Moreover, the above mentioned glassy polymers are soluble only in strong acids, and consequently not suitable candidates for membrane fabrication (Tullos et al., 1999). Therefore, the new strategies for the synthesis of rigid-rod polymers are mainly focused on increasing solubility and processability (Comesaña-Gándara, 2015).

In this regard, Park and co-workers (2010), based on the thermal conversion of imides containing hydroxides to benzoxazoles performed by Tullos and co-workers (1999)(Park et al., 2010) (Tullos et al., 1999), demonstrated the occurrence of free-volume structures in dense glassy polymers that can be systematically tailored by thermal rearrangement. This process enables an extraordinary gas separation performance and constitutes a novel method to prepare high-performance polymers for molecular-scale separations (Park et al., 2007). This successful research based on poly(1,3-benzoazole)s membranes was carried out by subjecting membranes to a thermal treatment in solid state of poly(o-hydroxyimide)s, containing *ortho* positioned functional groups (with respect to the amino group) (Díez et al., 2018) (Galizia et al., 2017). This thermal rearrangement processes involves a thermal cyclization step subjected to temperatures of 350-450 °C for a certain duration of time and under inert atmosphere or vacuum. The need for a thermal processing to manufacture these materials is responsible of their name as 'thermally rearranged', or TR polymers. Depending on the functional group in the ortho position (-OH, -SH, or -NH$_2$) of the precursor, the structures resulting from the cyclization process are PBO, PBT, PPL or PBI (Park et al., 2007)(Han et al., 2010)(Choi et al., 2010). Since polybenzoxazoles may be a source of possible cross-linking as a consequence of the high temperature used during their conversion, which would also explain their insolubility, this material cannot be processed. In this sense, TR-precursors during the manufacture of these membranes can be *ortho*-hydroxyl polyimides (HPI) and *ortho*-hydroxyl polyamides (HPA) (also called α-TR and β-TR polymers, respectively, HPIs being the most studied (Han et al., 2012). Figure 14, shows the solid-state mechanism of a poly(hydroxyimide) (PI) and a poly(hydroxyamide) (PA) to form a TR-polymer with the proposed PBOs structure.
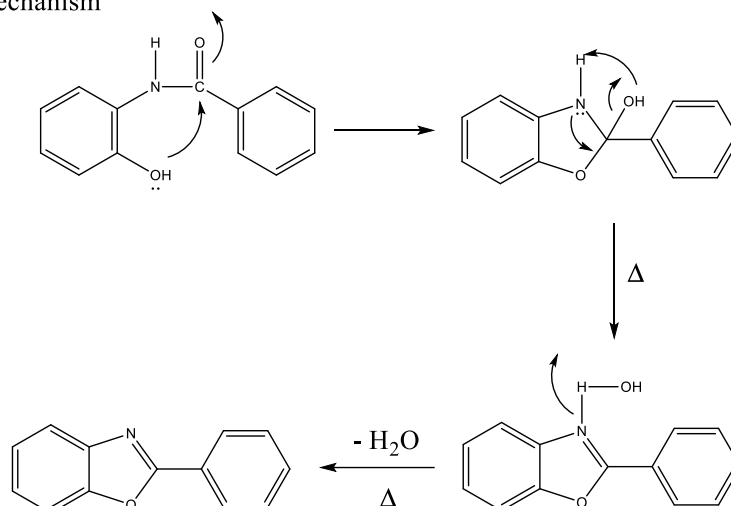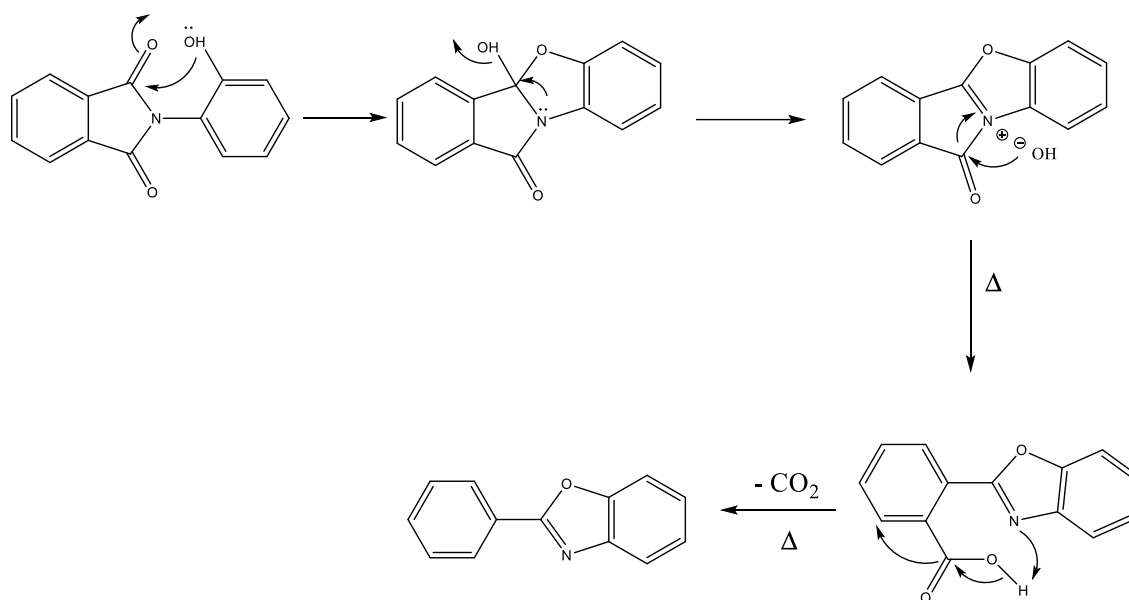
β-TR mechanism

α-TR-mechanism

Figure 14. General thermal rearrangement mechanism from HPAs to TR-PBOs (β-TRPBO) and from HPIs to TR-PBOs (α -TRPBO)

In both cases a final polyheterocycle of the polybenzoxazole type is reached by a cyclization process, where the heat treatment is carried out at different temperatures, depending on the TR-precursor. Additionally, the solid-state conversion process involves decarboxylation when the precursor is a polyimide, while the thermal reorganization phenomenon takes place through the loss of water molecules, or cyclodehydration, when

using a polyiamide as a precursor. The final PBO materials possess a chemically stable structure, resistance to CO_2 plasticization (likely due to their cross-linked structure) and excellent permeability and selectivity values due to the formation of a desirable free volume element distribution during thermal conversion (Smith et al., 2014) (Díez et al., 2018) (Calle et al., 2012) (Comesaña-Gándara et al., 2014).

Although in both cases the final structure of the PBO is similar, membranes exhibit different characteristics, especially in terms of gas transport properties. The TR precursor HPI can efficiently separate condensable gases, while the TR precursor HPA has an outstanding ability to separate light gases (Díez., 2014). In this context, the development of this thesis is mainly focused on the thermal rearrangement of the easily processable material HPA. These aromatic polyamides exhibit an appropriate balance of properties such as high thermal resistance, good mechanical and chemical stability and easier processability when their precursor monomers are adequately selected (De Abajo, et al., 1995).

Park and co-workers (2007) demonstrated that polymers with a medium cavity size, with a narrow cavity size distribution and a shape reminiscent of bottlenecks connecting adjacent chambers, possess high permeability and high selectivity (Park et al., 2007). Thus, TR-polymers provide an increase in FFV as a consequence of the generation of microcavities with controlled size bimodal distribution in the range of 0.3–0.4 nm (which is beneficial for selective transport of gas molecules such as CO_2) and 0.7–0.9 nm (which entails an enhanced gas diffusion) (Han et al., 2012). The above bimodal cavity size distribution is governed by the structure of the precursor and the protocol of thermal treatment used to produce the TR-PBO (Comesaña-Gándara, 2015).

Gas transport in TR-polymer membranes depends on the degree of thermal conversion, the nature of the free volume elements and their size distribution (Park et al., 2010). It is assumed that the newly created micropores mediating the transport of gases in TR polymers are responsible for the usual molecular screening in the separation of gases by glassy polymeric membranes. The narrowest part of these micropores plays a role of a molecular size caliber. Today, there are consistent empirical proofs confirming the exceptional selective molecular transport performance and high permselectivity in small molecules because of the free volume structure of these polymers.

In brief, the TRs obtained from HPA present a high permeability as well as high selectivity at elevated temperatures due to their enhanced cavity size distribution (Han et al., 2012). The increased free volume elements evolved by thermal rearrangement of PHAs are

expected to have superior transport properties for the separation of small gas and vapor molecules.

References

A. P. Cote, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O.M.Y., 2005. Porous, Crystalline, Covalent Organic Frameworks. Science (80-.). 310, 1164–1166. https://doi.org/10.1126/science.1118625

Abbas, H.F., Daud, W.M.A.W., 2010. Hydrogen production by methane decomposition : A review. Int. J. Hydrogen Energy 35, 1160–1190. https://doi.org/10.1016/j.ijhydene.2009.11.036

Abdin, Z., Zafaranloo, A., Rafiee, A., Mérida, W., Lipiński, W., Khalilpour, K.R., 2020. Hydrogen as an energy vector. Renew. Sustain. Energy Rev. 120, 109620. https://doi.org/10.1016/J.RSER.2019.109620

Achinas, S., Achinas, V., Euverink, G.J.W., 2017. A Technological Overview of Biogas Production from Biowaste. Engineering 3, 299–307. https://doi.org/10.1016/J.ENG.2017.03.002

Adewole, J.K., Ahmad, A.L., Ismail, S., Leo, C.P., 2013. Current challenges in membrane separation of CO2 from natural gas: A review. Int. J. Greenh. Gas Control 17, 46–65. https://doi.org/10.1016/j.ijggc.2013.04.012

Adhikari, S., Fernando, S., 2006. Hydrogen membrane separation techniques. Ind. Eng. Chem. Res. 45, 875–881. https://doi.org/10.1021/ie050644l

Aguilar-Lugo, C., Lee, W.H., Miguel, J.A., De La Campa, J.G., Prádanos, P., Bae, J.Y., Lee, Y.M., Álvarez, C., Lozano, Á.E., 2021. Highly Permeable Mixed Matrix Membranes of Thermally Rearranged Polymers and Porous Polymer Networks for Gas Separations. ACS Appl. Polym. Mater. 3, 5224–5235. https://doi.org/10.1021/acsapm.1c01012

Aguilar-Lugo, C., Suárez-García, F., Hernández, A., Miguel, J.A., Lozano, Á.E., De La Campa, J.G., Álvarez, C., 2019. New Materials for Gas Separation Applications: Mixed Matrix Membranes Made from Linear Polyimides and Porous Polymer Networks Having Lactam Groups. Ind. Eng. Chem. Res. 58, 9585–9595. https://doi.org/10.1021/acs.iecr.9b01402

Al-Mufachi, N.A., Rees, N. V., Steinberger-Wilkens, R., 2015. Hydrogen selective membranes: A review of palladium-based dense metal membranes. Renew. Sustain. Energy Rev. 47, 540–551. https://doi.org/10.1016/j.rser.2015.03.026

Andriani, D., Wresta, A., Atmaja, T.D., Saepudin, A., 2014. A Review on Optimization Production and Upgrading Biogas Through CO2 Removal Using Various Techniques. Appl. Biochem. Biotechnol. 172, 1909–1928. https://doi.org/10.1007/s12010-013-0652-x

Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H., Kougias, P.G., 2018. Biogas upgrading and utilization: Current status and perspectives. Biotechnol. Adv. 36, 452–466. https://doi.org/10.1016/j.biotechadv.2018.01.011

Aroon, M.A., Ismail, A.F., Matsuura, T., Montazer-Rahmati, M.M., 2010. Performance studies of mixed matrix membranes for gas separation: A review. Sep. Purif. Technol. 75, 229–242. https://doi.org/10.1016/j.seppur.2010.08.023

Baker, R.W., 2002. Future directions of membrane gas separation technology. Ind. Eng. Chem. Res. 41, 1393–1411. https://doi.org/10.1021/ie0108088

Baker, R.W., Lokhandwala, K., 2008. Natural gas processing with membranes: An overview. Ind. Eng. Chem. Res. 47, 2109–2121. https://doi.org/10.1021/ie071083w

Baker, R.W., Low, B.T., 2014. Gas separation membrane materials: A perspective. Macromolecules 47, 6999–7013. https://doi.org/10.1021/ma501488s

Bakonyi, P., Kumar, G., Nemestóthy, N., Lin, C.Y., Bélafi-Bakó, K., 2013a. Biohydrogen purification using a commercial polyimide membrane module: Studying the effects of some process variables. Int. J. Hydrogen Energy. https://doi.org/10.1016/j.ijhydene.2013.09.133

Bakonyi, P., Nemestóthy, N., Bélafi-Bakó, K., 2013b. Biohydrogen purification by membranes: An overview on the operational conditions affecting the performance of non-porous, polymeric and ionic liquid based gas separation membranes. Int. J. Hydrogen Energy. https://doi.org/10.1016/j.ijhydene.2013.05.158

Ball, M., Wietschel, M., 2009. The future of hydrogen - opportunities and challenges. Int. J. Hydrogen Energy 34. https://doi.org/10.1016/j.ijhydene.2008.11.014

Bandehali, S., Ebadi Amooghin, A., Sanaeepur, H., Ahmadi, R., Fuoco, A., Jansen, J.C., Shirazian, S., 2022. Polymers of intrinsic microporosity and thermally rearranged polymer membranes for highly efficient gas separation. Sep. Purif. Technol. https://doi.org/10.1016/j.seppur.2021.119513

Barrer, R.M., Rideal, E.K., 1939. Permeation, diffusion and solution of gases in organic polymers. Trans. Faraday Soc. 35, 628–643. https://doi.org/10.1039/tf9393500628

Bastani, D., Esmaeili, N., Asadollahi, M., 2013. Polymeric mixed matrix membranes containing zeolites as a filler for gas separation applications: A review. J. Ind. Eng. Chem. https://doi.org/10.1016/j.jiec.2012.09.019

Basu, S., Khan, A.L., Cano-Odena, A., Liu, C., Vankelecom, I.F.J., 2010. Membrane-based technologies for biogas separations. Chem. Soc. Rev. 39, 750–768. https://doi.org/10.1039/b817050a

Bauer, F., Hulteberg, C., Persson, T., Tamm, D., 2013. Biogas upgrading – Review of commercial technologies. (SGC Rapport; Vol. 270). Svenskt Gastekniskt Center AB.

Ben, T., Ren, H., Shengqian, M., Cao, D., Lan, J., Jing, X., Wang, W., Xu, J., Deng, F., Simmons, J.M., Qiu, S., Zhu, G., 2009. Targeted synthesis of a porous aromatic framework with high stability and exceptionally high surface area. Angew. Chemie - Int. Ed. 48, 9457–9460. https://doi.org/10.1002/anie.200904637

Bermejo, L.A., Alvarez, C., Maya, E.M., García, C., de la Campa, J.G., Lozano, A.E., 2018. Synthesis, characterization and gas separation properties of novel polyimides containing cardo and tert-butyl-m-terphenyl moieties. Express Polym. Lett. 12, 479–489. https://doi.org/10.3144/expresspolymlett.2018.40

Bernardo, P., Drioli, E., 2010. Membrane gas separation progresses for process intensification strategy in the petrochemical industry. Pet. Chem. 50, 271–282. https://doi.org/10.1134/S0965544110040043

Bernardo, P., Drioli, E., Golemme, G., 2009. Membrane Gas Separation: A Review/State of the Art. Ind. Eng. Chem. Res. 48, 4638–4663. https://doi.org/10.1021/ie8019032

Bernardo, P., Jansen, J.C., 2015. Polymeric membranes for the purification of hydrogen, in: V. Subramani, A. Basile, T.N.V. (Ed.), Compendium of Hydrogen Energy. Woodhead Publishing, Oxford., pp. 419–443. https://doi.org/10.1016/b978-1-78242-361-4.00014-5

Bharathiraja, B., Sudharsanaa, T., Bharghavi, A., Jayamuthunagai, J., Praveenkumar, R., 2016. Biohydrogen and Biogas – An overview on feedstocks and enhancement process. Fuel 185, 810–828. https://doi.org/10.1016/J.FUEL.2016.08.030

Biswal, B.P., Chaudhari, H.D., Banerjee, R., Kharul, U.K., 2016. Chemically Stable Covalent Organic Framework (COF)-Polybenzimidazole Hybrid Membranes: Enhanced Gas Separation through Pore Modulation. Chem. - A Eur. J. 22, 4695–4699. https://doi.org/10.1002/chem.201504836

BOE, 2021. Ley 7/2021, de 20 de mayo, de cambio climático y transición energética. Boletín Oficial del Estado., Boletín Oficial del Estado. Spain.

BOE, 2018. Resolución de 8 de octubre de 2018, de la Dirección General de Política Energética y Minas, por la que se modifican las normas de gestión técnica del sistema NGTS-06, NGTS-07 y los protocolos de detalle PD-01 y PD-02. Boletín Oficial del Estado., BOE. Spain.

Borjigin, H., Liu, Q., Zhang, W., Gaines, K., Riffle, J.S., Paul, D.R., Freeman, B.D., McGrath,

J.E., 2015a. Synthesis and characterization of thermally rearranged (TR) polybenzoxazoles: Influence of isomeric structure on gas transport properties. Polymer (Guildf). 75, 199–210. https://doi.org/10.1016/j.polymer.2015.07.024

Borjigin, H., Stevens, K.A., Liu, R., Moon, J.D., Shaver, A.T., Swinnea, S., Freeman, B.D., Riffle, J.S., McGrath, J.E., 2015b. Synthesis and characterization of polybenzimidazoles derived from tetraaminodiphenylsulfone for high temperature gas separation membranes. Polymer (Guildf). 71, 135–142. https://doi.org/10.1016/j.polymer.2015.06.021

Boudellal, M., 2018. Power-to-Gas: Renewable Hydrogen Economy for the Energy Transition. Walter de Gruyter GmbH & Co KG., Berlin, Boston.

Bowser, J.R., Williams, P.J., Kurz, K., 1983. Cleavage of Silicon-Nitrogen Bonds by Acid Chlorides: An Unusual Synthetic Route to Amides. J. Org. Chem. 48, 4111–4113. https://doi.org/10.1021/jo00170a050

Brunetti, A., Cersosimo, M., Kim, J.S., Dong, G., Fontananova, E., Lee, Y.M., Drioli, E., Barbieri, G., 2017. Thermally rearranged mixed matrix membranes for CO2 separation: An aging study. Int. J. Greenh. Gas Control 61, 16–26. https://doi.org/10.1016/j.ijggc.2017.03.024

Brunetti, A., Scura, F., Barbieri, G., Drioli, E., 2010. Membrane technologies for CO2 separation. J. Memb. Sci. 359, 115–125. https://doi.org/10.1016/j.memsci.2009.11.040

Budd, P.M., Msayib, K.J., Tattershall, C.E., Ghanem, B.S., Reynolds, K.J., McKeown, N.B., Fritsch, D., 2005. Gas separation membranes from polymers of intrinsic microporosity. J. Memb. Sci. https://doi.org/10.1016/j.memsci.2005.01.009

Bushell, A.F., Attfield, M.P., Mason, C.R., Budd, P.M., Yampolskii, Y., Starannikova, L., Rebrov, A., Bazzarelli, F., Bernardo, P., Carolus Jansen, J., Lanč, M., Friess, K., Shantarovich, V., Gustov, V., Isaeva, V., 2013. Gas permeation parameters of mixed matrix membranes based on the polymer of intrinsic microporosity PIM-1 and the zeolitic imidazolate framework ZIF-8. J. Memb. Sci. 427, 48–62. https://doi.org/10.1016/j.memsci.2012.09.035

Calle, M., Chan, Y., Jo, H.J., Lee, Y.M., 2012. The relationship between the chemical structure and thermal conversion temperatures of thermally rearranged (TR) polymers. Polymer (Guildf). 53, 2783–2791. https://doi.org/10.1016/j.polymer.2012.04.032

Carvalho, A.L., Maugeri, F., Silva, V., Hernández, A., Palacio, L., Pradanos, P., 2011. AFM analysis of the surface of nanoporous membranes: Application to the nanofiltration of potassium clavulanate. J. Mater. Sci. 46, 3356–3369. https://doi.org/10.1007/s10853-010-5224-7

Chen, Ying-pin, Bashir, Sajid, Liu, Louise, 2017. Nanostructured Materials for Next-Generation Energy Storage and Conversion. Hydrogen Production, Storage, and Utilization. Springer Nature, Germany, Berlin. https://doi.org/10.1007/978-3-662-53514-1

Chen, C.C., Qiu, W., Miller, S.J., Koros, W.J., 2011. Plasticization-resistant hollow fiber membranes for CO2/CH4 separation based on a thermally crosslinkable polyimide. J. Memb. Sci. 382, 212–221. https://doi.org/10.1016/j.memsci.2011.08.015

Chen, H.Z., Chung, T.S., 2012. CO2-selective membranes for hydrogen purification and the effect of carbon monoxide (CO) on its gas separation performance. Int. J. Hydrogen Energy 37, 6001–6011. https://doi.org/10.1016/j.ijhydene.2011.12.124

Cheng, X.Q., Konstas, K., Doherty, C.M., Wood, C.D., Mulet, X., Xie, Z., Ng, D., Hill, M.R., Shao, L., Lau, C.H., 2017. Hyper-Cross-Linked Additives that Impede Aging and Enhance Permeability in Thin Polyacetylene Films for Organic Solvent Nanofiltration. ACS Appl. Mater. Interfaces 9, 14401–14408. https://doi.org/10.1021/acsami.7b02295

Cheng, Y., Ying, Y., Japip, S., Jiang, S.D., Chung, T.S., Zhang, S., Zhao, D., 2018. Advanced

Porous Materials in Mixed Matrix Membranes. Adv. Mater. 30, 1–20. https://doi.org/10.1002/adma.201802401

Chiou, J.S., Paul, D.R., 1987. Effects of CO2 exposure on gas transport properties of glassy polymers. J. Memb. Sci. 32, 195–205. https://doi.org/10.1016/S0376-7388(00)85006-1

Choi, J.I., Jung, C.H., Han, S.H., Park, H.B., Lee, Y.M., 2010. Thermally rearranged (TR) poly(benzoxazole-co-pyrrolone) membranes tuned for high gas permeability and selectivity. J. Memb. Sci. 349, 358–368. https://doi.org/10.1016/j.memsci.2009.11.068

Chuah, C.Y., Jiang, X., Goh, K., Wang, R., 2021. Recent progress in mixed-matrix membranes for hydrogen separation. Membranes (Basel). https://doi.org/10.3390/membranes11090666

Chung, T.S., Jiang, L.Y., Li, Y., Kulprathipanja, S., 2007. Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. Prog. Polym. Sci. 32, 483–507. https://doi.org/10.1016/j.progpolymsci.2007.01.008

Comesaña-Gándara, B., 2015. Synthesis and Evaluation of Novel Materials for Gas Separation Membranes Through Thermal Rearrangement Processes of ortho - Funtionalized Polyimides. PhD Thesis. Institute of Polymer Science and Technology, CSIC.

Comesaña-Gandara, B., Ansaloni, L., Lee, Y.M., Lozano, A.E., De Angelis, M.G., 2017. Sorption, diffusion, and permeability of humid gases and aging of thermally rearranged (TR) polymer membranes from a novel ortho-hydroxypolyimide. J. Memb. Sci. 542, 439–455. https://doi.org/10.1016/j.memsci.2017.08.009

Comesaña-Gándara, B., Calle, M., Jo, H.J., Hernández, A., de la Campa, J.G., de Abajo, J., Lozano, A.E., Lee, Y.M., 2014. Thermally rearranged polybenzoxazoles membranes with biphenyl moieties: Monomer isomeric effect. J. Memb. Sci. 450, 369–379. https://doi.org/10.1016/j.memsci.2013.09.010

Comesaña-Gándara, B., Chen, J., Bezzu, C.G., Carta, M., Rose, I., Ferrari, M.C., Esposito, E., Fuoco, A., Jansen, J.C., McKeown, N.B., 2019. Redefining the Robeson upper bounds for CO2/CH4 and CO2/N2 separations using a series of ultrapermeable benzotriptycene-based polymers of intrinsic microporosity. Energy Environ. Sci. 12, 2733–2740. https://doi.org/10.1039/c9ee01384a

D.W. Breck., 1975. Zeolite Molecular Sieves: Structure, Chemistry and Use. Anal. Chim. Acta 75, 493. https://doi.org/10.1016/s0003-2670(01)85391-5

Das, D., Veziroglu, T.N., 2008. Advances in biological hydrogen production processes. Int. J. Hydrogen Energy 33, 6046–6057. https://doi.org/10.1016/j.ijhydene.2008.07.098

De Abajo, J., José G. de la Campa, Ángel E. Lozano, J.C.A., 1995. Thermally Stable Polymers: Novel Aromatic Polyamides. Adv. Mater. 148.151. https://doi.org/10.1201/b10862-5

De Abajo, J., De la Campa, J.G., Lozano, A.E., Espeso, J., García, C., 2003. Designing Aromatic Polyamides and Polyimides for Gas Separation Membranes. Macromol. Symp. 199, 293–306. https://doi.org/10.1002/masy.200350925

Dechnik, J., Gascon, J., Doonan, C.J., Janiak, C., Sumby, C.J., 2017. Mixed-Matrix Membranes. Angew. Chemie - Int. Ed. 56, 9292–9310. https://doi.org/10.1002/anie.201701109

Díaz, U., Corma, A., 2016. Ordered covalent organic frameworks, COFs and PAFs. From preparation to application. Coord. Chem. Rev. https://doi.org/10.1016/j.ccr.2015.12.010

Díez., B., 2014. Nuevos materiales de separación de gases formados mediante conversión térmica de polímeros aromáticos a polibenzoxazoles (TR-PBO). PhD Thesis. Univeristy of Valladolid.

Díez, B., Cuadrado, P., Marcos-Fernández, Á., de la Campa, J.G., Tena, A., Prádanos, P.,

Palacio, L., Lee, Y.M., Alvarez, C., Lozano, Á.E., Hernández, A., 2018. Thermally rearranged polybenzoxazoles made from poly(ortho-hydroxyamide)s. Characterization and evaluation as gas separation membranes. React. Funct. Polym. 127, 38–47. https://doi.org/10.1016/j.reactfunctpolym.2018.03.013

Ding, L.-X., Wei, Y., Li, L., Zhang, T., Wang, H., Xue, J., Ding, L.X., Wang, S., Caro, J., Gogotsi, Y., 2018. MXene molecular sieving membranes for highly efficient gas separation. Nat. Commun. 9. https://doi.org/10.1038/s41467-017-02529-6

Ding, S.-Y., Wang, W., 2013. Covalent organic frameworks (COFs): from design to applications. Chem. Soc. Rev 42, 548. https://doi.org/10.1039/c2cs35072f

Dong, G., Y.M.L., 2017. Thermally Rearranged Polymeric Membranes: Materials and Applications, in: E. Drioli, L. Giorno, E.F. (Ed.), Comprehensive Membrane Science and Engineering (Second Edition). Elsevier, Oxford, pp. 190–215.

Dong, G., Lee, Y.M., 2017. Microporous polymeric membranes inspired by adsorbent for gas separation. J. Mater. Chem. A 5 (26), 13294–13319. https://doi.org/10.1039/c7ta04015f

Dong, G., Li, H., Chen, V., 2013. Challenges and opportunities for mixed-matrix membranes for gas separation. J. Mater. Chem. A 1, 4610–4630. https://doi.org/10.1039/c3ta00927k

Doolittle, A.K., 1951. Studies in newtonian flow. II. the dependence of the viscosity of liquids on free-space. J. Appl. Phys. 22. https://doi.org/10.1063/1.1699894

EBA, 2018. EBA Statistical Report 2018. Brussels, Belgium. https://doi.org/10.1139/e11-014

EBA 2020, 2021. "Statical Report of the European Biogas Association 2020." Brussels, Belgium. https://doi.org/10.1080/0034408180130314

EBA 2021, 2021. Statistical Report of the European Biogas Association 2021. Brussels, Belgium.

Ebadi Amooghin, A., Mashhadikhan, S., Sanaeepur, H., Moghadassi, A., Matsuura, T., Ramakrishna, S., 2019. Substantial breakthroughs on function-led design of advanced materials used in mixed matrix membranes (MMMs): A new horizon for efficient CO 2 separation. Prog. Mater. Sci. 102, 222–295. https://doi.org/10.1016/j.pmatsci.2018.11.002

Edlund, D., 2009. Hydrogen Membrane Technologies and Application in Fuel Processing, in: Hydrogen and Syngas Production and Purification Technologies. https://doi.org/10.1002/9780470561256.ch8

Elbeshbishy, E., Dhar, B.R., Nakhla, G., Lee, H.S., 2017. A critical review on inhibition of dark biohydrogen fermentation. Renew. Sustain. Energy Rev. https://doi.org/10.1016/j.rser.2017.05.075

Espeso, J., Lozano, A.E., de la Campa, J.G., de Abajo, J., 2006. Effect of substituents on the permeation properties of polyamide membranes. J. Memb. Sci. 280, 659–665. https://doi.org/10.1016/j.memsci.2006.02.023

Esteban, N., Ferrer, M.L., Ania, C.O., De La Campa, J.G., Lozano, Á.E., Álvarez, C., Miguel, J.A., 2020. Porous Organic Polymers Containing Active Metal Centers for Suzuki-Miyaura Heterocoupling Reactions. ACS Appl. Mater. Interfaces 12, 56974–56986. https://doi.org/10.1021/acsami.0c16184

Etxeberria-Benavides, M., David, O., Johnson, T., Łozińska, M.M., Orsi, A., Wright, P.A., Mastel, S., Hillenbrand, R., Kapteijn, F., Gascon, J., 2018. High performance mixed matrix membranes (MMMs) composed of ZIF-94 filler and 6FDA-DAM polymer. J. Memb. Sci. 550, 198–207. https://doi.org/10.1016/j.memsci.2017.12.033

Flaconnèche, B., Martin, J., Klopffer, M.H., 2001. Transport Properties of Gases in Polymers: Experimental Methods. Oil Gas Sci. Technol. - Rev. IFP 56, 245–259. https://doi.org/10.2516/ogst:2001022

Freeman, B.D., 1999. Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes. Macromolecules 32, 375–380. https://doi.org/10.1021/ma9814548

Freeman, B.D., Pinnau, I., 2021. Gas and Liquid Separations Using Membranes: An Overview. UTC.

Galizia, M., Chi, W.S., Smith, Z.P., Merkel, T.C., Baker, R.W., Freeman, B.D., 2017. 50th Anniversary Perspective: Polymers and Mixed Matrix Membranes for Gas and Vapor Separation: A Review and Prospective Opportunities. Macromolecules 50, 7809–7843. https://doi.org/10.1021/acs.macromol.7b01718

Gao, X., Zou, X., Ma, H., Meng, S., Zhu, G., 2014. Highly selective and permeable porous organic framework membrane for CO_2 capture. Adv. Mater. 26, 3644–3648. https://doi.org/10.1002/adma.201400020

García, C., Lozano, A.E., De la Campa, J.G., De Abajo, J., 2003. Soluble polyimides from a new dianhydride: 5'-Tert-butyl-m-terphenyl-3,4,3",4"-tetracarboxylic acid dianhydride. Macromol. Rapid Commun. https://doi.org/10.1002/marc.200350014

García, C., Tiemblo, P., Lozano, A.E., De Abajo, J., De la Campa, J.G., 2002. Gas separation properties of new poly(aryl ether ketone)s with pendant groups. J. Memb. Sci. https://doi.org/10.1016/S0376-7388(02)00060-1

Gary R., M., 2014. Synthetic Nitrogen Production:A practical guide to the products and Processes. Kluwer Academic/Plenum Press, New York, USA. https://doi.org/10.1007/s13398-014-0173-7.2

Ghosal, K., Freeman, B.D., Chern, R.T., Alvarez, J.C., de la Campa, J.G., Lozano, A.E., de Abajo, J., 1995. Gas separation properties of aromatic polyamides with sulfone groups. Polymer (Guildf). 36, 793–800. https://doi.org/10.1016/0032-3861(95)93110-8

Glenk, G., Reichelstein, S., 2019. Economics of converting renewable power to hydrogen. Nat. Energy 4, 216–222. https://doi.org/10.1038/s41560-019-0326-1

Godula-Jopek, A., 2015. Hydrogen Production: By Electrolysis. Wiley VCH, Weinheim, Germany. https://doi.org/10.1002/9783527676507

Goh, P.S., Ismail, A.F., Sanip, S.M., Ng, B.C., Aziz, M., 2011. Recent advances of inorganic fillers in mixed matrix membrane for gas separation. Sep. Purif. Technol. 81, 243–264. https://doi.org/10.1016/j.seppur.2011.07.042

Gruber, E., 1978. L. G. E. Struik: Physical Aging in Amorphous Polymers and Other Materials. Elsevier Sci. Publ. Comp., Amsterdam-Oxford-New York 1978. 229 Seiten, 141 Abbildungen, Preis: US $ 42,50, Holl. Gulden 97,50. Berichte der Bunsengesellschaft für Phys. Chemie. https://doi.org/10.1002/bbpc.19780820975

H. Lin, B.D.F., 2006. Permeation and diffusion, in: H. Czichos, T. Saito, L.S. (Ed.), Springer Handbook of Materials Measurement Methods. Springer, Berlín, Germany, pp. 371–387. https://doi.org/10.1016/s1369-7021(06)71582-6

Han, S.H., Kwon, H.J., Kim, K.Y., Seong, J.G., Park, C.H., Kim, S., Doherty, C.M., Thornton, A.W., Hill, A.J., Lozano, Á.E., Berchtold, K.A., Lee, Y.M., 2012. Tuning microcavities in thermally rearranged polymer membranes for CO 2 capture. Phys. Chem. Chem. Phys. 14, 4365–4373. https://doi.org/10.1039/c2cp23729f

Han, S.H., Lee, J.E., Lee, K.J., Park, H.B., Lee, Y.M., 2010. Highly gas permeable and microporous polybenzimidazole membrane by thermal rearrangement. J. Memb. Sci. 357, 143–151. https://doi.org/10.1016/j.memsci.2010.04.013

Hao, D., Zhang, J., Lu, H., Leng, W., Ge, R., Dai, X., Gao, Y., 2014. Fabrication of a COF-5 membrane on a functionalized α-Al2O3 ceramic support using a microwave irradiation method. Chem. Commun. 50, 1462–1464. https://doi.org/10.1039/c3cc48065h

Hinchliffe, A.B., Porter, K.E., 2000. A comparison of membrane separation and distillation. Chem. Eng. Res. Des. https://doi.org/10.1205/026387600527121

Horn, N.R., Paul, D.R., 2011. Carbon dioxide plasticization and conditioning effects in thick vs. thin glassy polymer films. Polymer (Guildf). 52, 1619–1627. https://doi.org/10.1016/j.polymer.2011.02.007

Hou, R., Ghanem, B.S., Smith, S.J.D., Doherty, C.M., Setter, C., Wang, H., Pinnau, I., Hill, M.R., 2020. Highly permeable and selective mixed-matrix membranes for hydrogen separation containing PAF-1. J. Mater. Chem. A 8, 14713–14720. https://doi.org/10.1039/d0ta05071g

Hu, X.D., Jenkins, S.E., Min, B.G., Polk, M.B., Kumar, S., 2003. Rigid-Rod Polymers: Synthesis, Processing, Simulation, Structure, and Properties. Macromol. Mater. Eng. https://doi.org/10.1002/mame.200300013

Huang, N., Chen, X., Krishna, R., Jiang, D., 2015. Two-dimensional covalent organic frameworks for carbon dioxide capture through channel-wall functionalization. Angew. Chemie - Int. Ed. 54, 2986–2990. https://doi.org/10.1002/anie.201411262

Huang, X., Yao, H., Cheng, Z., 2017. Hydrogen separation membranes of polymeric materials, in: Chen YP., Bashir S., L.J. (Ed.), Nanostructured Materials for Next-Generation Energy Storage and Conversion: Hydrogen Production, Storage, and Utilization. Springer, Berlin. Heidelberg., pp. 85–116. https://doi.org/10.1007/978-3-662-53514-1_3

Hydrogen Europe, 2019. Hydrogen Europe Vision on the Role of Hydrogen and Gas Infrastructure on the Road Toward a Climate Neutral Economy - A Contribution to the Transition of the Gas Market.

IEA, 2019. The Future of Hydrogen. Seizing today's opportunities. International Energy Agency.

IEA, 2017. Special Report: Energy Access Outlook. From Poverty to Prosperity. International Energy Agency.

Intergovernmental Panel on Climate Change, 2015. Drivers, Trends and Mitigation. Clim. Chang. 2014 Mitig. Clim. Chang. 351–412. https://doi.org/10.1017/cbo9781107415416.011

IPCC, 2021. Summary for Policymakers. In: Climate Change 2021: The physical science basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. https://doi.org/10.1080/03736245.2010.480842

IRENA 2022 [WWW Document], 2022. URL https://www.irena.org/bioenergy

Ismail, A.F., Khulbe, K.C., Matsuura, T., 2015. Gas separation membranes: Polymeric and inorganic, Gas Separation Membranes: Polymeric and Inorganic. Springer New York, Ottawa, ON, Canada. https://doi.org/10.1007/978-3-319-01095-3

Jeon, Y.W., Lee, D.H., 2015. Gas membranes for CO2/CH4 (biogas) separation: A review. Environ. Eng. Sci. 32, 71–85. https://doi.org/10.1089/ees.2014.0413

Kaboorani, A., Riedl, B., Blanchet, P., Fellin, M., Hosseinaei, O., Wang, S., 2012. Nanocrystalline cellulose (NCC): A renewable nano-material for polyvinyl acetate (PVA) adhesive. Eur. Polym. J. 48, 1829–1837. https://doi.org/10.1016/j.eurpolymj.2012.08.008

Kertik, A., Wee, L.H., Pfannmöller, M., Bals, S., Martens, J.A., Vankelecom, I.F.J., 2017. Highly selective gas separation membrane using in situ amorphised metal-organic frameworks. Energy Environ. Sci. 10, 2342–2351. https://doi.org/10.1039/c7ee01872j

Khdhayyer, M.R., Esposito, E., Fuoco, A., Monteleone, M., Giorno, L., Jansen, J.C., Attfield, M.P., Budd, P.M., 2017. Mixed matrix membranes based on UiO-66 MOFs in the polymer of intrinsic microporosity PIM-1. Sep. Purif. Technol. 173, 304–313. https://doi.org/10.1016/j.seppur.2016.09.036

Kim, J.S., Moon, S.J., Wang, H.H., Kim, S., Lee, Y.M., 2019. Mixed matrix membranes with a thermally rearranged polymer and ZIF-8 for hydrogen separation. J. Memb. Sci. 582,

381–390. https://doi.org/10.1016/j.memsci.2019.04.029

Kim, S., Hou, J., Wang, Y., Ou, R., Simon, G.P., Seong, J.G., Lee, Y.M., Wang, H., 2018a. Highly permeable thermally rearranged polymer composite membranes with a graphene oxide scaffold for gas separation. J. Mater. Chem. A. https://doi.org/10.1039/c8ta02256a

Kim, S., Lee, Y.M., 2015. Rigid and microporous polymers for gas separation membranes. Prog. Polym. Sci. 43, 1–32. https://doi.org/10.1016/j.progpolymsci.2014.10.005

Kim, S., Shamsaei, E., Lin, X., Hu, Y., Simon, G.P., Seong, J.G., Kim, J.S., Lee, W.H., Lee, Y.M., Wang, H., 2018b. The enhanced hydrogen separation performance of mixed matrix membranes by incorporation of two-dimensional ZIF-L into polyimide containing hydroxyl group. J. Memb. Sci. 549, 260–266. https://doi.org/10.1016/j.memsci.2017.12.022

Kim, W.G., Zhang, X., Lee, J.S., Tsapatsis, M., Nair, S., 2012. Epitaxially grown layered MFI-bulk MFI hybrid zeolitic materials. ACS Nano 6, 9978–9988. https://doi.org/10.1021/nn3036254

Klotz, E.J.F., Claridge, T.D.W., Anderson, H.L., 2006. Homo- and hetero-[3]rotaxanes with two π-systems clasped in a single macrocycle. J. Am. Chem. Soc. 128, 15374–15375. https://doi.org/10.1021/ja0665139

Kohl, A.L., Nielsen, R.B., 1997. Gas purification 5th ed, Gulf Publishing Company. Elsevier, Houston. https://doi.org/10.1016/B978-088415220-0/50009-4

Konstas, K., Taylor, J.W., Thornton, A.W., Doherty, C.M., Lim, W.X., Bastow, T.J., Kennedy, D.F., Wood, C.D., Cox, B.J., Hill, J.M., Hill, A.J., Hill, M.R., 2012. Lithiated porous aromatic frameworks with exceptional gas storage capacity. Angew. Chemie - Int. Ed. 51, 6639–6642. https://doi.org/10.1002/anie.201201381

Koros, W.J., Fleming, G.K., 1993. Membrane-based gas separation. J. Memb. Sci. 83, 1–80. https://doi.org/10.1016/0376-7388(93)80013-N

Kougias, P.G., Angelidaki, I., 2018. Biogas and its opportunities—A review. Front. Environ. Sci. Eng. 12. https://doi.org/10.1007/s11783-018-1037-8

Kray, W.D., Rosser, R.W., 1977. Synthesis of Multifunctional Triarylfluoroethanes. 1. Condensation of Fluoro Ketones. J. Org. Chem. 42, 1186–1189. https://doi.org/10.1021/jo00427a018

Kumar, G., Bakonyi, P., Kobayashi, T., Xu, K.Q., Sivagurunathan, P., Kim, S.H., Buitrón, G., Nemestóthy, N., Bélafi-Bakó, K., 2016. Enhancement of biofuel production via microbial augmentation: The case of dark fermentative hydrogen. Renew. Sustain. Energy Rev. 57, 879–891. https://doi.org/10.1016/j.rser.2015.12.107

Kumar, S., 2015. Clean Hydrogen Production Methods. Springer, Berlín, Germany. https://doi.org/10.1007/978-3-319-14087-2

Kuppler, R.J., Timmons, D.J., Fang, Q.R., Li, J.R., Makal, T.A., Young, M.D., Yuan, D., Zhao, D., Zhuang, W., Zhou, H.C., 2009. Potential applications of metal-organic frameworks. Coord. Chem. Rev. https://doi.org/10.1016/j.ccr.2009.05.019

Lanč, M., Pilnáček, K., Mason, C.R., Budd, P.M., Rogan, Y., Malpass-Evans, R., Carta, M., Gándara, B.C., McKeown, N.B., Jansen, J.C., Vopička, O., Friess, K., 2019. Gas sorption in polymers of intrinsic microporosity: The difference between solubility coefficients determined via time-lag and direct sorption experiments. J. Memb. Sci. 570–571, 522–536. https://doi.org/10.1016/j.memsci.2018.10.048

Lau, C.H., Konstas, K., Doherty, C.M., Kanehashi, S., Ozcelik, B., Kentish, S.E., Hill, A.J., Hill, M.R., 2015. Tailoring Physical Aging in Super Glassy Polymers with Functionalized Porous Aromatic Frameworks for CO2 Capture. Chem. Mater. 27, 4756–4762. https://doi.org/10.1021/acs.chemmater.5b01537

Lau, C.H., Mulet, X., Konstas, K., Doherty, C.M., Sani, M.A., Separovic, F., Hill, M.R., Wood, C.D., 2016. Hypercrosslinked additives for ageless gas-separation membranes.

Angew. Chemie - Int. Ed. 55, 1998–2001. https://doi.org/10.1002/anie.201508070

Lau, C.H., Nguyen, P.T., Hill, M.R., Thornton, A.W., Konstas, K., Doherty, C.M., Mulder, R.J., Bourgeois, L., Liu, A.C.Y., Sprouster, D.J., Sullivan, J.P., Bastow, T.J., Hill, A.J., Gin, D.L., Noble, R.D., 2014. Ending aging in super glassy polymer membranes. Angew. Chemie - Int. Ed. 53, 5322–5326. https://doi.org/10.1002/anie.201402234

Lee, Y.M., Jung, C.H., Park, H.B., Kim, K.-Y., 2013. Preparation method of polybenooxazoles by thermal rearrangement, polybenzoxazoles prepared thereby, and gas separation membrane comprising the same. Patent No. US 8,618,244 B2.

Lenssen, N.J.L., Schmidt, G.A., Hansen, J.E., Menne, M.J., Persin, A., Ruedy, R., Zyss, D., 2019. Improvements in the GISTEMP Uncertainty Model. J. Geophys. Res. Atmos. 124, 6307–6326. https://doi.org/10.1029/2018JD029522

Li, P., Wang, Z., Qiao, Z., Liu, Y., Cao, X., Li, W., Wang, J., Wang, S., 2015. Recent developments in membranes for efficient hydrogen purification. J. Memb. Sci. https://doi.org/10.1016/j.memsci.2015.08.010

Li, S., Jo, H.J., Han, S.H., Park, C.H., Kim, S., Budd, P.M., Lee, Y.M., 2013. Mechanically robust thermally rearranged (TR) polymer membranes with spirobisindane for gas separation. J. Memb. Sci. 434, 137–147. https://doi.org/10.1016/j.memsci.2013.01.011

Li, X., Jiang, Z., Wu, Y., Zhang, H., Cheng, Y., Guo, R., Wu, H., 2015. High-performance composite membranes incorporated with carboxylic acid nanogels for CO2 separation. J. Memb. Sci. 495, 72–80. https://doi.org/10.1016/j.memsci.2015.07.065

Liao, D.C., Hsieh, K.H., 1994. Synthesis and characterization of bismaleimides derived from polyurethanes. J. Polym. Sci. Part A Polym. Chem. 32, 1665–1672. https://doi.org/10.1002/pola.1994.080320908

Liemberger, W., Groß, M., Miltner, M., Harasek, M., 2017. Experimental analysis of membrane and pressure swing adsorption (PSA) for the hydrogen separation from natural gas. J. Clean. Prod. 167, 896–907. https://doi.org/10.1016/j.jclepro.2017.08.012

Lin, R., Villacorta Hernandez, B., Ge, L., Zhu, Z., 2018. Metal organic framework based mixed matrix membranes: An overview on filler/polymer interfaces. J. Mater. Chem. A 6, 293–312. https://doi.org/10.1039/c7ta07294e

Liu, Q., Paul, D.R., Freeman, B.D., 2016. Gas permeation and mechanical properties of thermally rearranged (TR) copolyimides. Polymer (Guildf). 82, 378–391. https://doi.org/10.1016/j.polymer.2015.11.051

Lopez-Iglesias, B., Suárez-García, F., Aguilar-Lugo, C., González Ortega, A., Bartolomé, C., Martínez-Ilarduya, J.M., De La Campa, J.G., Lozano, Á.E., Álvarez, C., 2018. Microporous Polymer Networks for Carbon Capture Applications. ACS Appl. Mater. Interfaces 10, 26195–26205. https://doi.org/10.1021/acsami.8b05854

Lozano, A.E., de Abajo, J., de la Campa, J.G., 1997. Synthesis of aromatic polyisophthalamides by in situ silylation of aromatic diamines. Macromolecules 30, 2507–2508. https://doi.org/10.1021/ma961543p

Lozano, A.E., De Abajo, J., De La Campa, J.G., 1998. Quantum semiempirical study on the reactivity of silylated diamines in the synthesis of aromatic polyamides. Macromol. Theory Simulations 7, 41–48. https://doi.org/10.1002/(SICI)1521-3919(19980101)7:1<41::AID-MATS41>3.0.CO;2-G

Lu, W., Yuan, D., Zhao, D., Schilling, C.I., Plietzsch, O., Muller, T., Brase, S., Guenther, J., Blumel, J., Krishna, R., Li, Z., Zhou, H.C., 2010. Porous polymer networks: Synthesis, porosity, and applications in gas storage/separation. Chem. Mater. 22, 5964–5972. https://doi.org/10.1021/cm1021068

Luo, S., Zhang, Q., Zhu, L., Lin, H., Kazanowska, B.A., Doherty, C.M., Hill, A.J., Gao, P., Guo, R., 2018. Highly Selective and Permeable Microporous Polymer Membranes for Hydrogen Purification and CO2 Removal from Natural Gas. Chem. Mater. 30, 5322–

5332. https://doi.org/10.1021/acs.chemmater.8b02102

Ma, C., Urban, J.J., 2018. Polymers of Intrinsic Microporosity (PIMs) Gas Separation Membranes: A mini Review, in: Proceedings of the Nature Research Society. https://doi.org/10.11605/j.pnrs.201802002

Mahajan, R., Burns, R., Schaeffer, M., Koros, W.J., 2002. Challenges in Forming Successful Mixed Matrix Membranes with Rigid Polymeric Materials. J Appl Polym Sci 86, 881–890. https://doi.org/10.1002/app.10998

Mahajan, R., Koros, W.J., 2002. Mixed matrix membrane materials with glassy polymers. Part 1. Polym. Eng. Sci. 42, 1420–1431. https://doi.org/10.1002/pen.11041

Mahajan, R., Koros, W.J., 2000. Factors controlling successful formation of mixed-matrix gas separation materials. Ind. Eng. Chem. Res. 39, 2692–2696. https://doi.org/10.1021/ie990799r

Malakhov, A.O., Bazhenov, S.D., Vasilevsky, V.P., Borisov, I.L., Ovcharova, A.A., Bildyukevich, A.V., Volkov, V.V., Giorno, L., Volkov, A.V., 2019. Thin-film composite hollow fiber membranes for ethylene/ethane separation in gas-liquid membrane contactor. Sep. Purif. Technol. 219, 64–73. https://doi.org/10.1016/j.seppur.2019.02.053

Matteucci, S., Yampolskii, Y., Freeman, B.D., Pinnau, I., 2006. Transport of Gases and Vapors in Glassy and Rubbery Polymers. In: Yampolskii Y, Pinnau I, Freeman BD, editors. Materials science of membranes for gas and vapor separation, Materials Science of Membranes for Gas and Vapor Separation. John Wiley & Sons, Inc, Chichester. https://doi.org/10.1002/047002903X.ch1

Maya, E.M., García-Yoldi, I., Lozano, A.E., De La Campa, J.G., De Abajo, J., 2011. Synthesis, characterization, and gas separation properties of novel copolyimides containing adamantyl ester pendant groups. Macromolecules 44, 2780–2790. https://doi.org/10.1021/ma200093j

Mc Keown, N.B., Budd, P.M., 2006. Polymers of intrinsic microporosity (PIMs): Organic materials for membrane separations, heterogeneous catalysis and hydrogen storage. Chem. Soc. Rev. 35, 675–683. https://doi.org/10.1039/b600349d

McCaig, M.S., Paul, D.R., 2000. Effect of film thickness on the changes in gas permeability of a glassy polyarylate due to physical aging: Part I. Experimental observations. Polymer (Guildf). 41, 629–637. https://doi.org/10.1016/S0032-3861(99)00172-X

Merkel, T.C., He, Z., Pinnau, I., Freeman, B.D., Meakin, P., Hill, A.J., 2003. Sorption and Transport in Poly(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole-co-tetrafluoroethylene) Containing Nanoscale Fumed Silica. https://doi.org/10.1021/ma034975q

Miller, G. Q. and Stoecker, J., 1989. Selection of a hydrogen separation process, in: National Petroleum Refiners Association Annual Meeting, San Francisco, CA (USA). United States.

Mittal, V. (Ed.), 2019. Porous Polymer Networks (Specialty Materials), Vikas Mitt. ed. Central West Publishing, Orange NSW 2800, Australia.

Miyaura, N., Suzuki, A., 1995. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. Chem. Rev. 95, 2457–2483. https://doi.org/10.1021/cr00039a007

Mona, S., Kumar, S.S., Kumar, V., Parveen, K., Saini, N., Deepak, B., Pugazhendhi, A., 2020. Green technology for sustainable biohydrogen production (waste to energy): A review. Sci. Total Environ. 728, 138481. https://doi.org/10.1016/j.scitotenv.2020.138481

Monteleone, M., Esposito, E., Fuoco, A., Lanč, M., Pilnáček, K., Friess, K., Bezzu, C.G., Carta, M., McKeown, N.B., Jansen, J.C., 2018. A novel time lag method for the analysis of mixed gas diffusion in polymeric membranes by on-line mass spectrometry: Pressure dependence of transport parameters. Membranes (Basel). 8.

https://doi.org/10.3390/membranes8030073

Moore, T.T., Koros, W.J., 2005. Non-ideal effects in organic-inorganic materials for gas separation membranes. J. Mol. Struct. 739, 87–98. https://doi.org/10.1016/j.molstruc.2004.05.043

Muhammad Hussain, A.K., 2012. Mixed-Matrix Membrane for Gas Separation: Polydimethylsiloxane Filled with Zeolite. Chem. Eng. Techmology 35, 561–569. https://doi.org/10.1002/ceat.201100419

Muñoz, D.M., Calle, M., De La Campa, J.G., De Abaje, J., Lozane, A.E., 2009. An improved method for preparing very high molecular weight polyimides. Macromolecules 42, 5892–5894. https://doi.org/10.1021/ma9005268

Muñoz, D.M., De La Campa, J.G., De Abajo, J., Lozano, A.E., 2007. Experimental and theoretical study of an improved activated polycondensation method for aromatic polyimides. Macromolecules 40, 8225–8232. https://doi.org/10.1021/ma070842j

Muñoz, R., Meier, L., Diaz, I., Jeison, D., 2015. A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading. Rev. Environ. Sci. Biotechnol. 14, 727–759. https://doi.org/10.1007/s11157-015-9379-1

Naderi, A., Asadi Tashvigh, A., Chung, T.S., Weber, M., Maletzko, C., 2018. Molecular design of double crosslinked sulfonated polyphenylsulfone /polybenzimidazole blend membranes for an efficient hydrogen purification. J. Memb. Sci. 563, 726–733. https://doi.org/10.1016/j.memsci.2018.06.033

Nasir, R., Mukhtar, H., Man, Z., Mohshim, D.F., 2013. Material Advancements in Fabrication of Mixed-Matrix Membranes. Chem. Eng. Technol. https://doi.org/10.1002/ceat.201200734

Navarro, O., Kelly, R.A., Nolan, S.P., 2003. A General Method for the Suzuki-Miyaura Cross-Coupling of Sterically Hindered Aryl Chlorides: Synthesis of Di-and Tri-ortho-substituted Biaryls in 2-Propanol at Room Temperature. https://doi.org/10.1021/ja038631r

Nik, O.G., Chen, X.Y., Kaliaguine, S., 2012. Functionalized metal organic framework-polyimide mixed matrix membranes for CO 2/CH 4 separation. J. Memb. Sci. 413–414, 48–61. https://doi.org/10.1016/j.memsci.2012.04.003

Noble, R.D., 2011. Perspectives on mixed matrix membranes. J. Memb. Sci. 378, 393–397. https://doi.org/10.1016/j.memsci.2011.05.031

Ockwig, N.W., Nenoff, T.M., 2007. Membranes for hydrogen separation. Chem. Rev. 107, 4078–4110. https://doi.org/10.1021/cr0501792

Oishi, Y., Kakimoto, M.A., Imai, Y., 1988. Synthesis of Aromatic Polyamides from N,N'-Bis (trimethylsilyl)-Substituted Aromatic Diamines and Aromatic Diacid Chlorides. Macromolecules 21, 547–550. https://doi.org/10.1021/ma00181a001

Olah, G.A., 1993. superelectrophiles. Angew. Chemie - Int. Ed. English 32, 767–922.

Ozturk, B., Demirciyeva, F., 2013. Comparison of biogas upgrading performances of different mixed matrix membranes. Chem. Eng. J. 222, 209–217. https://doi.org/10.1016/j.cej.2013.02.062

Park, H.B., Han, S.H., Jung, C.H., Lee, Y.M., Hill, A.J., 2010. Thermally rearranged (TR) polymer membranes for CO2 separation. J. Memb. Sci. 359, 11–24. https://doi.org/10.1016/j.memsci.2009.09.037

Park, H.B., Jung, C.H., Lee, Y.M., Hill, A.J., Pas, S.J., Mudie, S.T., Van Wagner, E., Freeman, B.D., Cookson, D.J., 2007. Polymers with Cavities Tuned for Fast Selective Transport of Small Molecules and Ions. Science (80-.). 318, 254–258. https://doi.org/10.1126/science.1146744

Park, K.S., Ni, Z., Côté, A.P., Choi, J.Y., Huang, R., Uribe-Romo, F.J., Chae, H.K., O'Keeffe Michael, Yaghi, O.M., 2006. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks, in: Proceedings of the National Academy of Sciences of the

United States of America. pp. 10186–10191. https://doi.org/10.1073/pnas.0602439103

Paul, D.R., Kemp, D.R., 1973. Containing Adsorptive Fillers. J. Polym. Sci. Polym. Symp. 93, 79–93.

Paul, D.R., Pixton, M.R., Paul, D.R., 1994. Relationships Between Structure and Transport Properties for Polymers with Aromatic Backbones. In: Paul DR, Yampolskii Y, editors. Polymeric gas separation membranes., in: Polymeric Gas Separation Membranes. Boca Raton, pp. 83–154. https://doi.org/10.1201/9781351075886-3

Pearson, G., Leary, M., Subic, A., Wellnitz, J., 2011. Performance Comparison of Hydrogen Fuel Cell and Hydrogen Internal Combustion Engine Racing Cars, in: S. Hung, A. Subic, J.W. (Ed.), Sustainable Automotive Technologies 2011. Springer Berlín, Heidelberg, Heidelberg, Berlín, pp. 85–91. https://doi.org/10.1007/978-3-642-19053-7_11

Peramanu, S., Cox, B.G., Pruden, B.B., 1999. Economics of hydrogen recovery processes for the purification of hydroprocessor purge and off-gases. Int. J. Hydrogen Energy 24, 405–424. https://doi.org/10.1016/S0360-3199(98)00105-0

Perry, J.D., Nagai, K., Koros, W.J., 2006. Polymer membranes for hydrogen separations. MRS Bull. 31, 745–749. https://doi.org/10.1557/mrs2006.187

Petersson, A., Wellinger, A., 2009. Biogas upgrading technologies – developments and innovations Task 37 -Energy from biogas and landfill gas IeA Bioenergy aims to accelerate the use of environmental sound and cost-competitive Bioenergy on a sustainable basis, and thereby achieve a substant. IEA Bioenergy 13.

Phan, A., Doonan, C.J., Uribe-Romo, F.J., Knobler, C.B., Okeeffe, M., Yaghi, O.M., 2009. Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks. Acc. Chem. Res. 43, 58–67. https://doi.org/10.1021/ar900116g

Ramírez-Morales, J.E., Tapia-Venegas, E., Nemestóthy, N., Bakonyi, P., Bélafi-Bakó, K., Ruiz-Filippi, G., 2013. Evaluation of two gas membrane modules for fermentative hydrogen separation. Int. J. Hydrogen Energy 38, 14042–14052. https://doi.org/10.1016/j.ijhydene.2013.08.092

Ramírez-Morales, J.E., Tapia-Venegas, E., Toledo-Alarcón, J., Ruiz-Filippi, G., 2015. Simultaneous production and separation of biohydrogen in mixed culture systems by continuous dark fermentation. Water Sci. Technol. 71, 1271–1285. https://doi.org/10.2166/wst.2015.104

Recio, R., Palacio, L., Prádanos, P., Hernández, A., Lozano, Á.E., Marcos, Á., de la Campa, J.G., de Abajo, J., 2007. Gas separation of 6FDA-6FpDA membranes. Effect of the solvent on polymer surfaces and permselectivity. J. Memb. Sci. 293, 22–28. https://doi.org/10.1016/j.memsci.2007.01.022

Rezakazemi, M., Ebadi Amooghin, A., Montazer-Rahmati, M.M., Ismail, A.F., Matsuura, T., 2014. State-of-the-art membrane based CO2 separation using mixed matrix membranes (MMMs): An overview on current status and future directions. Prog. Polym. Sci. 39, 817–861. https://doi.org/10.1016/j.progpolymsci.2014.01.003

Rico-Martínez, S., Álvarez, C., Hernández, A., Miguel, J.A., Lozano, Á.E., 2022. Mixed Matrix Membranes Loaded with a Porous Organic Polymer Having Bipyridine Moieties. Membranes (Basel). 12, 547. https://doi.org/10.3390/membranes12060547

Rittmann, S., Herwig, C., 2012. A comprehensive and quantitative review of dark fermentative biohydrogen production. Microb. Cell Fact. 11, 20–25. https://doi.org/10.1186/1475-2859-11-115

Robeson, L.M., 2008. The upper bound revisited. J. Memb. Sci. 320, 165–185. https://doi.org/10.1016/j.memsci.2008.04.030

Robeson, L.M., 1991. Correlation of separation factor versus permeability for polymeric membranes. J. Memb. Sci. 62, 165–185. https://doi.org/10.1016/0376-7388(91)80060-

J

Robeson, L.M., Burgoyne, W.F., Langsam, M., Savoca, A.C., Tien, C.F., 1994. High performance polymers for membrane separation. Polymer (Guildf). 35, 4970–4978. https://doi.org/10.1016/0032-3861(94)90651-3

Rowe, B.W., Freeman, B.D., Paul, D.R., 2009. Physical aging of ultrathin glassy polymer films tracked by gas permeability. Polymer (Guildf). 50, 5565–5575. https://doi.org/10.1016/j.polymer.2009.09.037

Rutherford, S.W., Do, D.D., 1997. Review of time lag permeation technique as a method for characterisation of porous media and membranes. Adsorption 3, 283–312. https://doi.org/10.1007/BF01653631

Ryckebosch, E., Drouillon, M., Vervaeren, H., 2011. Techniques for transformation of biogas to biomethane. Biomass and Bioenergy 35, 1633–1645. https://doi.org/10.1016/J.BIOMBIOE.2011.02.033

Sanaeepur, H., Kargari, A., 2015. Modeling and Analysis Cellulose acetate/nano-porous zeolite mixed matrix membrane for CO 2 separation. | Greenh. Gas Sci Technol 5, 291–304. https://doi.org/10.1002/ghg

Sanders, D.F., Smith, Z.P., Guo, R., Robeson, L.M., McGrath, J.E., Paul, D.R., Freeman, B.D., 2013. Energy-efficient polymeric gas separation membranes for a sustainable future: A review. Polymer (Guildf). 54, 4729–4761. https://doi.org/10.1016/j.polymer.2013.05.075

Sanders, D.F., Smith, Z.P., Ribeiro, C.P., Guo, R., McGrath, J.E., Paul, D.R., Freeman, B.D., 2012. Gas permeability, diffusivity, and free volume of thermally rearranged polymers based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA). J. Memb. Sci. 409–410, 232–241. https://doi.org/10.1016/j.memsci.2012.03.060

Sazali, N., Salleh, W.N.W., Ismail, A.F., 2020. Synthetic polymer-based membranes for hydrogen separation, in: Synthetic Polymeric Membranes for Advanced Water Treatment, Gas Separation, and Energy Sustainability. Elsevier, pp. 273–292. https://doi.org/10.1016/b978-0-12-818485-1.00012-5

Schorer, L., Schmitz, S., Weber, A., 2019. Membrane based purification of hydrogen system (MEMPHYS). Int. J. Hydrogen Energy 44, 12708–12714. https://doi.org/10.1016/J.IJHYDENE.2019.01.108

Scipioni, A., Manzardo, A., Ren, J., 2017. Hydrogen Economy: Supply Chain, Life Cycle Analysis and Energy Transition for Sustainability. Academic Press, London, UK.

Semino, R., Ramsahye, N.A., Ghoufi, A., Maurin, G., 2016. Microscopic Model of the Metal-Organic Framework/Polymer Interface: A First Step toward Understanding the Compatibility in Mixed Matrix Membranes. ACS Appl. Mater. Interfaces 8, 809–819. https://doi.org/10.1021/acsami.5b10150

Sheldon M., Wiederhorn, Richard J. Fields, Samuel Low, Gun-Woong Bahng, Alois Wehrstedt, Junhee Hahn, Yo Tomota, Takashi Miyata, Haiqing Lin, Benny D. Freeman, Shuji Aihara, Yukito Hagihara, Tetsuya Tagawa.Sheldon M. Wiederhorn, Richard J. Fields, Samuel, T.T., 2006. Mechanical Properties, in: H. Czichos, L.E. Smith, T.S. (Ed.), Handbook of Materials Measurement Methods. Berlin, Heidelberg.

Shimekit, B., Mukhtar, H., Murugesan, T., 2011. Prediction of the relative permeability of gases in mixed matrix membranes. J. Memb. Sci. 373, 152–159. https://doi.org/10.1016/j.memsci.2011.02.038

Shine, K.P., Fuglestvedt, J.S., Hailemariam, K., Stuber, N., 2005. Comparing Climate Impacts of Emissions of Greenhouse Gases. Clim. Chang. 68, 281–302.

Singh, A., Freeman, B.D., Pinnau, I., 1998. Pure and Mixed Gas Acetone/ Nitrogen Permeation Properties of Polydimethylsiloxane [PDMS], J Polym Sci B: Polym Phys. John Wiley & Sons, Inc.

Sircar, S., Golden, T.C., 2009. Pressure Swing Adsorption Technology for Hydrogen Production, in: K. Liu, C. Song, V.S. (Ed.), Hydrogen and Syngas Production and Purification Technologies. John Wiley & Sons., New York, USA., pp. 414–450. https://doi.org/10.1002/9780470561256.ch10

Smith, S.J.D., Hou, R., Lau, C.H., Konstas, K., Kitchin, M., Dong, G., Lee, J., Lee, W.H., Seong, J.G., Lee, Y.M., Hill, M.R., 2019. Highly permeable Thermally Rearranged Mixed Matrix Membranes (TR-MMM). J. Memb. Sci. 585, 260–270. https://doi.org/10.1016/j.memsci.2019.05.046

Smith, Z.P., Czenkusch, K., Wi, S., Gleason, K.L., Hernández, G., Doherty, C.M., Konstas, K., Bastow, T.J., Álvarez, C., Hill, A.J., Lozano, A.E., Paul, D.R., Freeman, B.D., 2014. Investigation of the chemical and morphological structure of thermally rearranged polymers. Polymer (Guildf). 55, 6649–6657. https://doi.org/10.1016/j.polymer.2014.10.055

Smith, Z.P., Hernández, G., Gleason, K.L., Anand, A., Doherty, C.M., Konstas, K., Alvarez, C., Hill, A.J., Lozano, A.E., Paul, D.R., Freeman, B.D., 2015. Effect of polymer structure on gas transport properties of selected aromatic polyimides, polyamides and TR polymers. J. Memb. Sci. 493, 766–781. https://doi.org/10.1016/j.memsci.2015.06.032

Smith, Z.P., Sanders, D.F., Ribeiro, C.P., Guo, R., Freeman, B.D., Paul, D.R., McGrath, J.E., Swinnea, S., 2012. Gas sorption and characterization of thermally rearranged polyimides based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA). J. Memb. Sci. 415–416, 558–567. https://doi.org/10.1016/j.memsci.2012.05.050

Soto, C., Aguilar Lugo, C., Rodríguez, S., Palacio, L., Lozano, E., Prádanos, P., Hernandez, A., 2020. Enhancement of CO2/CH4 permselectivity via thermal rearrangement of mixed matrix membranes made from an o-hydroxy polyamide with an optimal load of a porous polymer network. Sep. Purif. Technol. 247, 116895. https://doi.org/10.1016/j.seppur.2020.116895

Soto, C., Torres-Cuevas, E.S., González-Ortega, A., Palacio, L., Lozano, Á.E., Freeman, B.D., Prádanos, P., Hernández, A., 2021a. Gas separation by mixed matrix membranes with porous organic polymer inclusions within o-hydroxypolyamides containing m-terphenyl moieties. Polymers (Basel). 13. https://doi.org/10.3390/polym13060931

Soto, C., Torres-Cuevas, E.S., González-Ortega, A., Palacio, L., Prádanos, P., Freeman, B.D., Lozano, Á.E., Hernandez, A., 2021b. Hydrogen recovery by mixed matrix membranes made from 6fcl-apaf hpa with different contents of a porous polymer network and their thermal rearrangement. Polymers (Basel). 13. https://doi.org/10.3390/polym13244343

Sridhar, S., Bee, S., Bhargava, S., 2014. Membrane-based Gas Separation: Principle, Applications and Future Potential. Chem. Eng. Dig. 1, 1–25.

Sridhar, S., Smitha, B., Aminabhavi, T.M., 2007. Separation of carbon dioxide from natural gas mixtures through polymeric membranes - A review. Sep. Purif. Rev. 36, 113–174. https://doi.org/10.1080/15422110601165967

Stanislowski, J.J., Holmes, M.J., Snyder, A.C., Tolbert, S.G., Curran, T.J., 2013. Advanced CO2 separation technologies: Coal gasification, warm-gas cleanup, and hydrogen separation membranes. Energy Procedia 37, 2316–2326. https://doi.org/10.1016/j.egypro.2013.06.113

Strathmann, H., 2001. Membrane separation processes: Current relevance and future opportunities. AIChE J. 47, 1077–1087. https://doi.org/10.1002/aic.690470514

Struik, L., 1978. Physical aging in amorphous polymers and other materials. Polym. Eng. Sci. 17, 165–173.

Surya Prakash, G.K., Panja, C., Shakhmin, A., Shah, E., Mathew, T., Olah, G.A., Loker, K.B.,

2009. BF 3-H 2 O Catalyzed Hydroxyalkylation of Aromatics with Aromatic Aldehydes and Dicarboxaldehydes: Efficient Synthesis of Triarylmethanes, Diarylmethylbenzaldehydes, and Anthracene Derivatives. J. Org. Chem 74, 8659. https://doi.org/10.1021/jo901668j

Suzuki, A., 1999. Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles, 1995-1998. J. Organomet. Chem. https://doi.org/10.1016/S0022-328X(98)01055-9

Swaidan, R., Ghanem, B., Litwiller, E., Pinnau, I., 2015a. Physical Aging, Plasticization and Their Effects on Gas Permeation in "rigid" Polymers of Intrinsic Microporosity. Macromolecules 48, 6553–6561. https://doi.org/10.1021/acs.macromol.5b01581

Swaidan, R., Ghanem, B., Pinnau, I., 2015b. Fine-Tuned Intrinsically Ultramicroporous Polymers Redefine the Permeability/Selectivity Upper Bounds of Membrane-Based Air and Hydrogen Separations. ACS Macro Lett. 4, 947–951. https://doi.org/10.1021/acsmacrolett.5b00512

Tapia-Venegas, E., Ramirez-Morales, J.E., Silva-Illanes, F., Toledo-Alarcón, J., Paillet, F., Escudie, R., Lay, C.H., Chu, C.Y., Leu, H.J., Marone, A., Lin, C.Y., Kim, D.H., Trably, E., Ruiz-Filippi, G., 2015. Biohydrogen production by dark fermentation: scaling-up and technologies integration for a sustainable system. Rev. Environ. Sci. Biotechnol. https://doi.org/10.1007/s11157-015-9383-5

Tena, A., 2013. Phase-segregated Copoly (ether-imide)s, Optimization of Structure and Composition for gas separation applications. PhD Thesis. Univerisity of Valladolid. University of Valladolid.

Tena, A., de la Viuda, M., Palacio, L., Prádanos, P., Marcos-Fernández, Á., Lozano, Á.E., Hernández, A., 2014. Prediction of gas permeability of block-segregated polymeric membranes by an effective medium model. J. Memb. Sci. 453, 27–35. https://doi.org/10.1016/j.memsci.2013.10.023

Teplyakov, V. V., Durgar'yan, S.G., 1984. Correlation analysis of the gas permeability parameters of polymers. Polym. Sci. U.S.S.R. 26, 1678–1688. https://doi.org/10.1016/S0032-3950(84)80058-1

Thornton, A.W., Nairn, K.M., Hill, A.J., Hill, J.M., 2009. New relation between diffusion and free volume: I. Predicting gas diffusion. J. Memb. Sci. 338. https://doi.org/10.1016/j.memsci.2009.03.053

Thuan Lu, H., Li, W., Soroodan Miandoab, E., Kanehashi, S., Hu, G., 2020. The opportunity of membrane technology for hydrogen purification in the power to hydrogen (P2H) roadmap: a review. https://doi.org/10.1007/s11705-020-1983-0

Tien-Binh, N., Vinh-Thang, H., Chen, X.Y., Rodrigue, D., Kaliaguine, S., 2016. Crosslinked MOF-polymer to enhance gas separation of mixed matrix membranes. J. Memb. Sci. 520, 941–950. https://doi.org/10.1016/j.memsci.2016.08.045

Tiwari, R.R., Jin, J., Freeman, B.D., Paul, D.R., 2017. Physical aging, CO2 sorption and plasticization in thin films of polymer with intrinsic microporosity (PIM-1). J. Memb. Sci. 537, 362–371. https://doi.org/10.1016/j.memsci.2017.04.069

Toledo-Cervantes, A., Estrada, J.M., Lebrero, R., Muñoz, R., 2017. A comparative analysis of biogas upgrading technologies: Photosynthetic vs physical/chemical processes. Algal Res. 25, 237–243. https://doi.org/10.1016/J.ALGAL.2017.05.006

Tullos, G.L., Powers, J.M., Jeskey, S.J., Mathias, L.J., 1999. Thermal Conversion of Hydroxy-Containing Imides to Benzoxazoles: Polymer and Model Compound Study. https://doi.org/10.1021/ma981579c

Ullah Khan, I., Hafiz Dzarfan Othman, M., Hashim, H., Matsuura, T., Ismail, A.F., Rezaei-DashtArzhandi, M., Wan Azelee, I., 2017. Biogas as a renewable energy fuel – A review of biogas upgrading, utilisation and storage. Energy Convers. Manag. 150, 277–294. https://doi.org/10.1016/J.ENCONMAN.2017.08.035

Villalobos, L.F., Hilke, R., Akhtar, F.H., Peinemann, K.V., 2018. Fabrication of Polybenzimidazole/Palladium Nanoparticles Hollow Fiber Membranes for Hydrogen Purification. Adv. Energy Mater. 8. https://doi.org/10.1002/aenm.201701567

Vinh-Thang, H., Kaliaguine, S., 2013. Predictive models for mixed-matrix membrane performance: A review. Chem. Rev. 113, 4980–5028. https://doi.org/10.1021/cr3003888

Vinoba, M., Bhagiyalakshmi, M., Alqaheem, Y., Alomair, A.A., Pérez, A., Rana, M.S., 2017. Recent progress of fillers in mixed matrix membranes for CO2 separation: A review. Sep. Purif. Technol. https://doi.org/10.1016/j.seppur.2017.07.051

Vogel, H., Marvel, C.S., 1961. Polybenzimidazoles, new thermally stable polymers. J. Polym. Sci. 50, 511–539. https://doi.org/10.1002/pol.1961.1205015419

Voldsund, M., Jordal, K., Anantharaman, R., 2016. Hydrogen production with CO2 capture. Int. J. Hydrogen Energy. https://doi.org/10.1016/j.ijhydene.2016.01.009

Wang, H., Chung, T.S., Paul, D.R., 2014. Thickness dependent thermal rearrangement of an ortho-functional polyimide. J. Memb. Sci. 450, 308–312. https://doi.org/10.1016/j.memsci.2013.09.006

Wang, J., Yin, Y., 2017. Pretreatment of organic wastes for hydrogen production, in: J. Wang, Y.Y. (Ed.), Biohydrogen Production from Organic Wastes. Springer Singapore, Singapore, pp. 123–195. https://doi.org/10.1007/978-981-10-4675-9_4

Wang, R., Shi, L., Tang, C.Y., Chou, S., Qiu, C., Fane, A.G., 2010. Characterization of novel forward osmosis hollow fiber membranes. J. Memb. Sci. 355, 158–167. https://doi.org/10.1016/J.MEMSCI.2010.03.017

Wang, Y., Low, Z.X., Kim, S., Zhang, H., Chen, X., Hou, J., Seong, J.G., Lee, Y.M., Simon, G.P., Davies, C.H.J., Wang, H., 2018. Functionalized Boron Nitride Nanosheets: A Thermally Rearranged Polymer Nanocomposite Membrane for Hydrogen Separation. Angew. Chemie - Int. Ed. 57. https://doi.org/10.1002/anie.201809126

WBA, 2019. Global potential of biogas, World Biogas Association.

Weber, A.Z., Lipman, T.E., 2019. Fuel Cells and Hydrogen Production: Introduction, in: T.E. Lipman, A.Z.W. (Ed.), Fuel Cells and Hydrogen Production: A Volume in the Encyclopedia of Sustainability Science and Technology, Second Edition. Springer New York, New York, NY, pp. 1–8. https://doi.org/10.1007/978-1-4939-7789-5_1051

Weger, L., Abánades, A., Butler, T., 2017. Methane cracking as a bridge technology to the hydrogen economy. Int. J. Hydrogen Energy 42, 720–731. https://doi.org/10.1016/j.ijhydene.2016.11.029

Wind, J.D., Staudt-Bickel, C., Paul, D.R., Koros, W.J., 2002. The Effects of Crosslinking Chemistry on CO2 Plasticization of Polyimide Gas Separation Membranes. Ind. Eng. Chem. Res 41, 45. https://doi.org/10.1021/ie0204639

Wu, A.X., Drayton, J.A., Smith, Z.P., 2019. The perfluoropolymer upper bound. AIChE J. https://doi.org/10.1002/aic.16700

Wu, A.X., Lin, S., Mizrahi, K., Benedetti, F.M., Joo, T., Grosz, A.F., Storme, K.R., Roy, N., Syar, D., Smith, P., 2021. Revisiting group contribution theory for estimating fractional free volume of microporous polymer membranes. J. Memb. Sci. 636, 119526. https://doi.org/10.1016/j.memsci.2021.119526

Wu, H., Kruczek, B., Thibault, J., 2018. Impact of measuring devices and data analysis on the determination of gas membrane properties. J. Membr. Sci. Res. 4, 4–14. https://doi.org/10.22079/jmsr.2017.63433.1136

Wu, X., Tian, Z., Wang, S., Peng, D., Yang, L., Wu, Y., Xin, Q., Wu, H., Jiang, Z., 2017. Mixed matrix membranes comprising polymers of intrinsic microporosity and covalent organic framework for gas separation. J. Memb. Sci. 528, 273–283. https://doi.org/10.1016/j.memsci.2017.01.042

Xia, J., Chung, T.S., Paul, D.R., 2014. Physical aging and carbon dioxide plasticization of thin

polyimide films in mixed gas permeation. J. Memb. Sci. 450, 457–468. https://doi.org/10.1016/j.memsci.2013.09.047

Yampolskii, Y., 2012. Polymeric gas separation membranes. Macromolecules 45, 3298–3311. https://doi.org/10.1021/ma300213b

Yang, G., Guo, H., Kang, Z., Zhao, L., Feng, S., Jiao, F., Mintova, S., 2019. Green Hydrogen Separation from Nitrogen by Mixed-Matrix Membranes Consisting of Nanosized Sodalite Crystals. ChemSusChem 12, 4529–4537. https://doi.org/10.1002/cssc.201802577

Yang, Q., Li, L., Tan, W., Sun, Y., Wang, H., Ma, J., Zhao, X., 2017. Exceptional high selectivity of hydrogen/methane separation on a phosphonate-based MOF membrane with exclusion of methane molecules. Chem. Commun. 53, 9797–9800. https://doi.org/10.1039/c7cc05486f

Ying, Y., Cheng, Y., Peh, S.B., Liu, G., Shah, B.B., Zhai, L., Zhao, D., 2019. Plasticization resistance-enhanced CO2 separation at elevated pressures by mixed matrix membranes containing flexible metal-organic framework fillers. J. Memb. Sci. 582, 103–110. https://doi.org/10.1016/j.memsci.2019.03.088

Zhang, Q., Hu, J., Lee, D.J., 2016. Biogas from anaerobic digestion processes: Research updates. Renew. Energy 98, 108–119. https://doi.org/10.1016/j.renene.2016.02.029

Zhang, Y., Feng, X., Yuan, S., Zhou, J., Wang, B., 2016. Challenges and recent advances in MOF-polymer composite membranes for gas separation. Inorg. Chem. Front. 3, 896–909. https://doi.org/10.1039/c6qi00042h

Zimmerman, C.M., Singh, A., Koros, W.J., 1997. Tailoring mixed matrix composite membranes for gas separations. J. Memb. Sci. 137, 145–154. https://doi.org/10.1016/S0376-7388(97)00194-4

Chapter 2

Aims and Scope of the Thesis

2.1. Problem under investigation

The increase in CO_2 concentration in the atmosphere due to anthropogenic activities is nowadays accepted as the main cause of global warming. Therefore, there is an urgent need to reduce, or at least control, the emissions of CO_2 and other greenhouse gases. The gradual substitution of fossil fuels by renewable energies will certainly contribute to reduce CO_2 emissions. Wind and solar power have been intensively installed worldwide in the past decade, while biogas and biohydrogen are regarded as green substitutes of natural gas. Biogas and biohydrogen can be generated from renewable sources and exhibit a low CO_2 footprint. However, both gas biofuels need a purification (mainly CO_2 removal) prior to their injection into the natural gas grid or their use as fuel in vehicles. Gas phase separation using membranes is one of the fastest growing techniques in biogas upgrading, due to the limited footprint of their installations, high energy efficiency and economic advantages. Among the wide range of gas separation membranes, polymeric membranes have been proved to be very competitive, and dominate the market as a result of the combination of good processability, low price, ease of scale-up and ability to adjust their composition to the target application.

The limitations of existing conventional membranes in gas separation have opened up a wide range of research areas in the search for improved membrane performance, the key requirement for using new materials in industrial gas separation being processability. Organic, inorganic or hybrid materials have been added to polymers to form materials known as Mixed Matrix Membranes in order to take advantage of the processability of polymers and overcome the permeability-selectivity trade-off. In addition, polymers that are capable of forming benzoxazoles have been used to produce thermally rearranged mixed matrix membranes.

However, the performance of MMMs still suffers from defects caused by the poor contact between the polymer and the particle surface used as filler. Indeed, the voids that appear in the interfacial region as a result of the manufacturing process allow a direct gas flow through these channels, resulting in high gas permeability without improving selectivity.

There is a wide range of polymers used as a continuous phase to manufacture mixed matrix membranes. The most widely used to date are the so-called Polyimides (PI) due to their high gas separation performance, excellent mechanical properties and high thermal stability. However, PI are negatively affected by highly soluble gases such as CO_2, making them very prone to plasticization. In this context, polyamides (PA) exhibit a promising potential as an alternative polymeric matrix to support a good adhesion with particles. Despite PA have been poorly investigated in the field of MMMs, these polymers have several

properties that can improve polymer-filler adhesion and thus be excellent alternative candidates in the field of gas separation. In addition, PA have excellent mechanical and thermal properties and are easily processable materials.

On the other hand, zeolites have been the most widely used as the dispersed phase. However, Zeolites typically experience a poor polymer-filler adhesion, which becomes a real challenge in the development of defect-free mixed matrix membranes. In this thesis, new materials such as porous polymer networks (PPNs) have been developed as fillers for the manufacture of MMMs. PPNs have demonstrated an excellent polymer-filler adhesion, thus improving gas separation. To obtain excellent gas separation performances and meet the proposed objective, polymer-filler adhesion has also been studied in order to obtain defect-free MMMs. Finally, thermal rearrangement of MMMs has also been employed in order to achieve better gas permeation properties.

2.2. Research objectives

The main objective of this thesis is the manufacture and characterization of MMMs and their corresponding β-TR-MMMs for the separation of CO_2 from biogas and biohydrogen. This overall objective will be fulfilled by using the following specific objectives:

1. To obtain new polymeric materials capable of forming membranes with high free volume fraction and improved gas separation performance.

2. To develop mixed matrix membranes using the combination of polyamides and a new generation of porous polymer networks.

3. To develop thermally rearranged mixed matrix membranes.

4. To characterize the physical and chemical properties of the developed MMMs and β-TR-MMMs.

5. To evaluate the performance of the newly developed membranes in term of permeability and ideal selectivity for the separation of CO_2 from biogas and H_2 in biohydrogen.

6. To test other gas separations to characterization the new membranes as comprehensively as possible.

2.3. Scope of Study

Overcoming the current challenges of manufacturing gas separation membranes with a high performance to be employed at industrial scale implying overcoming the trade-off between permeability and selectivity. In this thesis, novel MMMs were developed by incorporating PPNs particles within a HPA capable to produce benzoxazoles, in order to separate CO_2 and H_2 from biogas and biohydrogen, respectively. This goal was achieved using the following approach:

1. *Development of new polymers with high free volume fraction and good thermal and mechanical properties*

This task aimed at exploring the synthesis of polymers capable of generating benzoxazoles to form TR-polymers, which have attracted considerable attention as a promising candidate for future applications in the CO_2 gas separation processes from biogas and biohydrogen, owing to their remarkable gas separation performance. The HPA precursor was selected based on its fairly low TR temperature, the expected high conversion rate (>90%) at lower temperatures (300 °C) and the fact that it decomposes at a high temperature (>500 ∘C).

2. *Manufacture of polyamides-porous polymer networks mixed matrix membranes*

In this context, the present PhD thesis is focused on taking advantage of the properties of a PA (as continuous phase) to produce benzoxazole adding a porous filler (as disperse phase) to form MMMs, which has been shown to improve membrane permeability and/or selectivity compared to pure polymers. Different PPNs loading, ranging from 10 to 40% wt, were used in order to manufacture the MMMs used in this study. The effect of PPN loading on the polymeric matrix and the influence of the manufacturing process on the morphology -and consequently on the performance- of the formed MMMs was herein investigated

3. *Fabrication of thermal rearrangement mixed matrix membranes*

The MMMs manufactured were subjected to a heat treatment of up to 375 °C in order to obtain a higher performance in gas separation, mainly for several gas pairs including the CO_2/CH_4 and H_2/CO_2 pairs.

4. *Evaluation of polyamides-porous polymer networks mixed matrix membranes*

The gas separation performance of the manufactured MMMs and their corresponding β-TR-MMMs represented the major aspects explored in this thesis. The capacity and performance of the developed MMMs were evaluated in terms of H_2, CO_2 and CH_4 permeability.

2.4. Thesis Overview

This PhD thesis was divided into six chapters. Chapter 1 provides a brief introduction of biogas and biohydrogen purification technologies, with a special focus on membrane separation technology (where the background on the fundamentals of gas transport phenomena in a film were included), MMMs as novel polymeric membrane materials, their morphologies as well as the factors that influence their morphology during their manufacture. Additionally, a brief summary of the main materials used as a filler to manufacture MMMs and TR-polymers was included in Chapter 1. The problem under investigation, thesis objectives and scope of the thesis are summarized in Chapter 2. Chapter 3 describes specific details about the materials used and experimental procedures. Chapter 4 explores the potential of the MMMs and their corresponding TR-MMMs to separate CO_2 from biogas, using a HPA as a polymeric matrix and a new family of PPNs as a filler. The thermal transitions, structure changes, mechanical properties and gas permeation properties of the films were compared. Chapter 5 assessed the influence of the HPA as a precursor of the MMMs and TR-MMMs in order to explore their potential to separate H_2 and CO_2 in biohydrogen. Moreover, membranes loaded up to 30% were analyzed by SEM and AFM, confirming fairly flat, low-scale surfaces with limited roughness. Chapter 6 describes the enhancement in gas permeation properties via synthesis of a new family of polyamides from a series of *m*-tertphenil-3, 3'-dicarboxylic acids with different substituent at position 5' obtained through the Suzuki-Miyaura reaction. MMMs and TR-MMMs were compared in terms of the permeability versus selectivity during the separation of H_2/CH_4 and H_2/N_2 gas pairs. Finally, Chapter 7 summarizes the main conclusions and future work recommendations derived from this thesis.

Chapter 3

Materials and Methods

3.1. Materials

The polymers used in this study include Polyamides (PA). The monomers 2,2-bis(3-amino-4-hydroxy phenyl)-hexafluoropropane (APAF), 4,4'-(hexafluoroisopropylidene) dianiline (6FpDA) were purchased from Apollo Scientific (Stockport, Cheshire, UK). APAF and 6FpDA were purified by sublimation at 220–225 °C and 180 °C respectively, before use. 2,2-bis(4-carboxyphenyl)hexafluoropropane (6F) (98%) was also purchased from Apollo Scientific. The reagents required to synthesize the diamines 3-(Methoxycarbonyl)phenylboronic acid (97%), 4-(Methoxycarbonyl)phenylboronic acid (97%) and 1,3-dibromo-5-tert-butylbenzene (99.55%) were purchased from Cymit quimica (Barcelona, Spain). Other reagents including NaOH (sodium hydroxide), sulfuric acid (H_2SO_4), tetrakis(triphenylphosphine) palladium(0) (Pd(PPh$_3$)$_4$), potassium carbonate (K_2CO_3), hydrochloric acid (HCl) and thionyl chloride (SOCl$_2$) were obtained from Scharlab (Barcelona, Spain) and used as received. Thionyl chloride (SOCl$_2$, 99.5%), chlorotrimethylsilane (CTMS, 98%), anhydrous pyridine (Py, 99.8%), N,N-dimethylaminopyridine (DMAP, 99%), anhydrous N,N-dimethylacetamide (DMAc, 99.8%), N- methyl-2-Pyrrolidinone (NMP, 99.5%), Tetrahydrofuran (THF, 99.9%) and chloroform (CHCl$_3$, 99.8%) were purchased from MilliporeSigma (Burlington, Massachusetts, USA) and were used as received. N,N-dimethylformamide (DMF, 99.8%) and Dimethylsulphoxide (DMSO, 99.8%) were purchased from Scharlab and were used as received. Purified nitrogen (99.999%) was provided by Air Liquide (Paris, France).

3.2. Synthesis of meta-terphenyldicarboxylic monomers

This section contains the general concepts of the previous synthesis of molecular structures corresponding to some monomers (used in chapter 6 of this thesis), based on the Suzuki-Miyaura coupling reaction (Fig. 1).
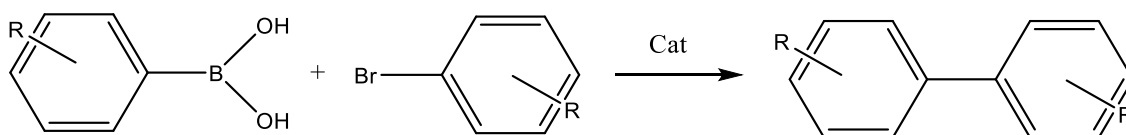

Figure 1. General scheme of Suzuki-Miyaura coupling reaction.

The Suzuki-Miyaura coupling reaction is a metal-catalyzed reaction between an alkynyl (vinyl), aryl, or alkynyl organoborate and a halide or triflate under basic conditions. This reaction is used to generate carbon-carbon (C-C) bonds obtaining conjugated systems of

alkenes, styrenes or biaryl compounds (Miyaura and Suzuki, 1995)(Suzuki, 1999). The reaction mechanism consists of three stages: i) oxidative addition, ii) transmetallation and iii) reductive elimination (regeneration of the catalyst and obtaining the coupling product) (Fig. 2).
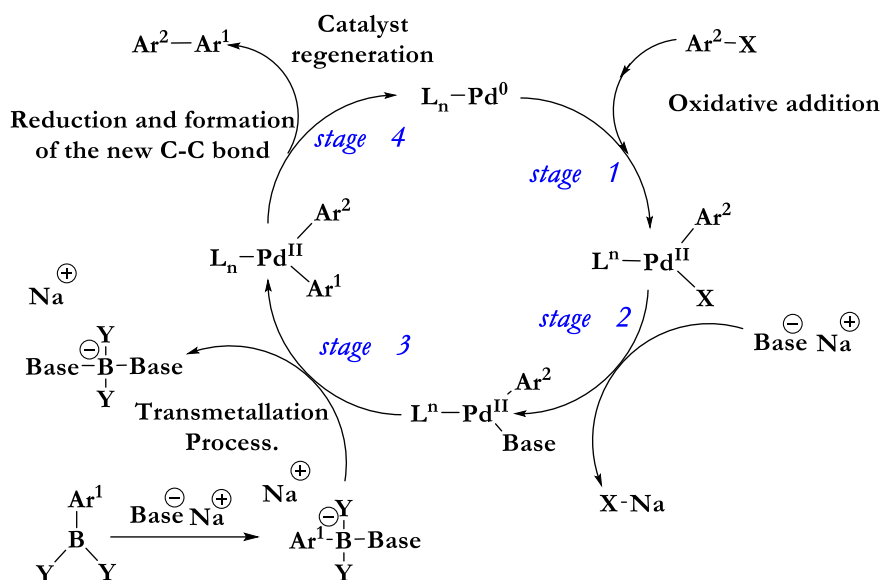

Figure 2. Simplified catalytic scheme of the Suzuki-Miyaura coupling reaction

Oxidative addition determines the rate in the catalytic cycle. This first step consists of an oxidative addition of R'X to the Pd0 complex, resulting in a new PdII intermediate with halogen and Ar2 as ligands. Then, transmetallation is initiated by a base to facilitate the transfer of the aryl or alkyl group from the organoborate to the palladium complex. Finally, the process of reductive elimination occurs, where an interaction between the two orbitals of the ligands to be eliminated must take place. Therefore, ligand position must be in a relative *cis* position. If the ligands are in *trans* position, this elimination could not be carried out (Navarro et al., 2003).

A meta-terphenyl isomer was used to carry out these reactions in this PhD thesis. Terphenyl is a polycyclic hydrocarbon consisting of a central benzene ring with two phenyl substituents and possessing extended delocalization. This delocalization makes these compounds highly thermally stable. The substitution of the molecule with two carboxyl groups allows further functionalization to more reactive acid chlorides, which can result into polyamides in polymerization reactions when reacting with compounds containing diamines.

3.3. Synthesis of the polymer matrix

The main objective of this PhD thesis is to manufacture high performance gas separation MMMs able to withstand thermal transposition changes. In this context, this chapter compiles the concepts and general methodology of the synthesis of different polyamides (continuous phase) and fillers (disperse phase) used for the manufacture of MMMs and β-TR-MMMs, techniques of characterization and transport properties, as well as a detailed protocol for membrane preparation in order to facilitate the understanding of the experimental work conducted.

A high molecular weight in the polymers ensures sufficiently robust membranes with good mechanical properties, and therefore suitable for gas separation applications. In this sense, the Carothers equation is used to correlate the extent of the reaction to the average degree of polymerization (DP) (Eq. 1):

$$DP = \frac{r+1}{r+1-2pr} \qquad\qquad (Eq.\ 8)$$

where p is the progress of the reaction (conversion), r is the stoichiometric imbalance defined as the ratio between the initial number of reactive groups of the monomers Eq_A and Eq_B, present in the medium, $r = \dfrac{Eq_A}{Eq_B}$ $(1 \geq r > 0)$. The maximum theoretical degree of polymerization will be infinite only when $r = 1$ (equivalence of functional groups) and the reaction conversion is complete. In this context: an exact stoichiometry of the functional groups, an optimal reaction conditions (ensuring a very high yield) and a high purity monomer are key factors in order to obtain polymers with high DP and consequently a high molecular weight. The presence of impurities negatively influences the degree of polymerization, which hinders the achievement of optimal conditions for the formation of a polymer. In addition, other factors inducing lower molecular weight during polymer synthesis are: i) The reaction of water with the dianhydride, resulting in non-reactive acid compounds leading to a stoichiometric disproportion; ii) the partial oxidation of the diamines resulting in the formation of mono-functional monomers or non-reactive molecules, iii) This species, together with side reactions from the hydrolysis of the amide solvents, generate aliphatic amines that can compete with the diamine monomer. Therefore, the use of high purity and anhydrous solvents, and inert atmospheres, are important factors to consider in this type of polymerization (Tena, 2013).

On the other hand, the polycondensation process often used for polymer synthesis can be impaired, decreasing its reactivity due to the difficulty of eliminating the leaving group in the reaction, and generating reversible reactions. "Polycondensation in melt", "interfacial polycondensation" and "polycondensation in solution" are the most commonly used techniques. Polycondensation in solution is characterized by the fact that the reaction is carried out in a homogeneous phase, which facilitates the rapid mixing of the reagents, thus favoring the contact between the functional groups. In this regard, the solvent used must be capable of dissolving both the monomers and the polymer formed until the reaction is complete or until a sufficiently high molecular weight has been obtained. Solvent selection plays a key role based on its ability to transfer and dissipate heat in polymerization. Indeed, the use of a non-adequate solvent could hinder the progress of the reaction. Polar aprotic organic solvents with high dielectric constant (ε) and a certain basic character such as N,N-dimethylformamide (DMF), Anhydrous N,N-dimethylacetamide (DMAc), N- methyl-2-Pyrrolidinone (NMP), Tetrahydrofuran (THF) are typically used in the manufacture of aromatic polyamides in solution. Finally, the polycondensation method can be carried out at low temperature (below ambient temperature) or at high temperature (≥ 100 °C). In this thesis, the polycondensation reaction was performed at low temperature.

Polycondensation reaction in solution at low temperature

It has been consistently proved that the most effective method for the preparation of polyamides was polycondensation solution at low temperature, which consists in a condensation reaction between an acid dichloride and a diamine. Several researchers have demonstrated that aliphatic polyamides can be prepared with excellent yields from silylated diamines and aliphatic acid chlorides(Bowser et al., 1983) (Lozano et al., 1997). For instance, Imai and coworkers (1988) found that trimethylsilyl diamines tend to be more reactive in combination with acid dichlorides than the corresponding unsilylated diamines (Oishi et al., 1988). The easy hydrolysis of diamines has led to the formation of silylated diamines *in situ* by addition of trimethylsilyl chloride (TMSC) to the diamine solution prior to the addition of acid dichloride. Several studies performing *in situ* diamine activation have shown that a stoichiometric amount of TMSC is not necessary to produce significant increases in the molecular weight of the polymer obtained (Lozano et al., 1997) (Díez et al., 2018) (Muñoz et al., 2007). Moreover, the *in situ* activation method exhibits additional benefits such as: i) The high reactivity of TMSC to water leads to the protection of the reagents from possible side reactions such as hydrolysis of acid chlorides, allowing the functionality of the monomers

throughout the reaction time; and ii) Simplification of the polyamidation techniques by avoiding isolation of silylated diamines.

In this PhD thesis, the use of base-assisted *in situ* silylation (as a catalyst) as a low-temperature activated polycondensation method was employed throughout the synthesis of polyamide, using diamines and acid dichlorides (Fig. 3a). The general synthesis of *in situ* silylated polyamides is illustrated in Fig. 3b.
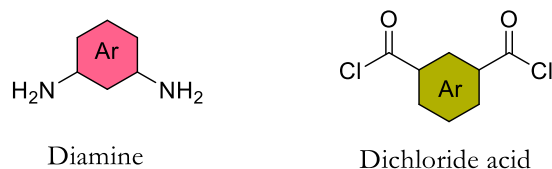

Figure 3a. General structure of diamines and dichloride's acid employed in this thesis
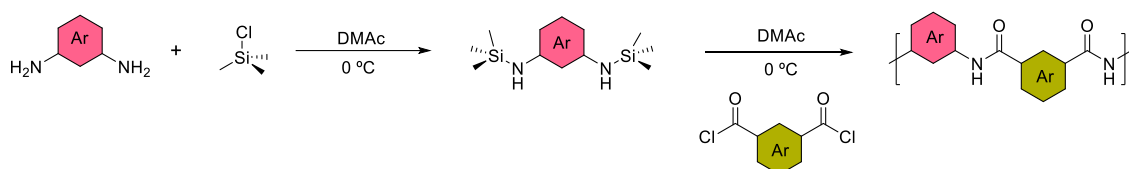
Figure 3b. General reaction mechanism by polycondensation in solution at low temperature with *in situ* silylation of aromatic diamine

The i*n situ* silylation method is being adopted in order to increase the reactivity of the diamines, leading to an increase in the molecular weight of the PA obtained. This method is based on the use of CTMS and a base such as pyridine (Py), in order to promote the silylation of diamine, and small amounts of a highly-nucleophilic cobase such as *N,N*-dimethylaminopyridine (DMAP) as polycondensation promoters. The silylated aromatic diamine tends to be more nucleophilic than the non-silylated ones, which favors the transfer of the electron density of the amine to the dianhydride moiety. This activation reaction is most advantageous for diamines of low reactivity, i.e., those with electron-withdrawing groups. This transfer opens the anhydride cycle simultaneously with the elimination of the trimethylsilyl group (Comesaña-Gándara, 2015).

Overall, the synthesis of PA is based on an amidation reaction, which consists of the nucleophilic addition of diamine nitrogen to the low electron density center of the carbonyl carbon of an acid derivative, with subsequent elimination of a low molecular weight molecule (Díez., 2014).

The polymers used in this thesis were synthesized via polycondensation reaction. All synthesis were carried out under a nitrogen atmosphere.

3.4. Synthesis of the filler

A new generation of PPNs were used as a disperse phase in the preparation of MMMs in this PhD Thesis. PPNs were obtained in quantitative yield by reacting rigid trifunctional aromatic monomers with two ketones containing electron-withdrawing groups in superacidic media. A new synthesis mechanism for PPNs, described in the literature as hydroxyalkylation reaction, has been proposed where a ketone or an aldehyde is protonated with an acid catalyst, and the resulting "ion" acts as an electrophile for aromatic substitution. The acid-catalyzed (Lewis or Brönsted) low-temperature condensation of ketones or aldehydes with aromatic compounds generates trisubstituted alcohols, in which the hydroxyl group is protonated. These trisubstituted alcohols are subjected to a subsequent reaction with an arene molecule to generate the corresponding triarylmethane derivatives (Surya Prakash et al., 2009)(Lopez-Iglesias et al., 2018).

On the other hand, superelectrophiles (electron deficient compounds that tend to accept electrons in reactions) under superacidic conditions are able to carry out a subsequent protonation or protosolvation of the protonated aldehydes or ketones. This generates super electrophilic or dipositive (doubly electron deficient) intermediates, significantly exceeding the reactivity of their parent monocations under conventional reaction conditions(Olah, 1993). Superelectrophilic intermediates can undergo continuous condensation reactions with weaker nucleophiles, making the reaction possible even with deactivated aromatic rings (Lopez-Iglesias et al., 2018).

Regardless of the reaction mechanism, the presence of electron-withdrawing groups (EWGs) favors the reactivity of the protonated carbonyl group. For example, superacid-catalyzed condensation reactions produced by superacids of trifluoromethylated ketones with somewhat deactivated aromatic hydrocarbons generate diaryl derivatives with high yields (Kray and Rosser, 1977). Therefore for the synthesis of three-dimensional cross-linked networks (termed PPNs), both amorphous and rigid, reactions of trifunctional aromatic molecules having specific symmetry and activated ketones acting as bifunctional monomers have been considered (Lopez-Iglesias et al., 2018).

3.5. Film formation

The polymer membranes were prepared by a dissolution-evaporation process, which consists of the dissolution of the polymer and subsequent evaporation of the solvent on glass plates, previously equilibrated on a heating plate. Three series of membranes were

manufactured in this study, to compare the properties: Homogeneous-membranes (precursor of MMMs) used as reference membrane, MMMs and TR-membranes.

3.5.1. Homogeneous membranes

The polymer matrix (or precursor of MMMs) was dissolved in 10% of NMP or THF used as a solvent. This homogeneous solution was filtered through a 3.1 μm polytetrafluoroethylene (PTFE) syringe filter and casted on a well-leveled glass (Fig. 4). The membranes prepared we subjected to a heat treatment in order to remove progressively the solvent: 60 °C overnight followed by 2 h at 80 °C on the plate (without vacuum), 1 h at 100 °C, 2 h at 120 °C and finally 12 h at 180 °C under vacuum to evaporate the residual solvent.
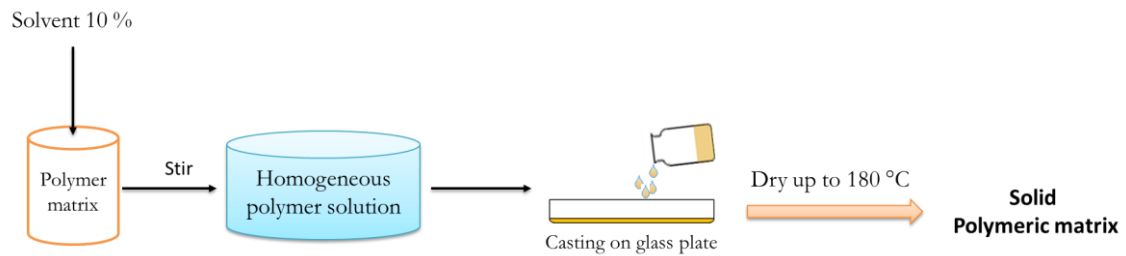

Figure 4. Manufacture of the membrane used as a reference membrane

3.5.2. Mixed Matrix Membranes

The above procedure was followed for the dissolution of the polymeric matrix. Simultaneously, the target percentage of the filler (disperse phase) was dispersed in NMP or THF overnight and then sonicated for 20 min (40 cycles of 20 s sonication using 30% as maximum amplitude) in order to completely disperse the particles (Fig. 5). The loading of filler was calculated based on Eq. 2.

$$Filler\ loading\ \left(wt\%\right) = \frac{w_{filler}}{w_{polymer} + w_{filler}} \cdot 100 \qquad (Eq.\ 9)$$

where w_{filler} and $w_{polymer}$ are the weight of polymer and filler, respectively.

Prior to dispersion in the bulk polymer, the priming method was employed, which consist in coating the surface of the filler with a polymer solution (Aroon et al., 2010). In this technique, a small percentage of the total polymer was added to the particle suspension and allowed to sonicate for 5 minutes, thus promoting an effective contact between the two

phases, before adding the disperse phase into the continuous phase. The homogeneous suspension was agitated for 2 hours. Then, the MMM obtained was casted on a leveled glass and subjected to the same heat treatment than the fabrication of HPA-membranes, in order to remove the solvent, heating up to 180 °C under vacuum. The thickness of the membranes obtained ranged from 40 to 60 µm. In all cases, suitable film uniformity was verified by measuring the film thickness standard deviation, which was lower than 5%.
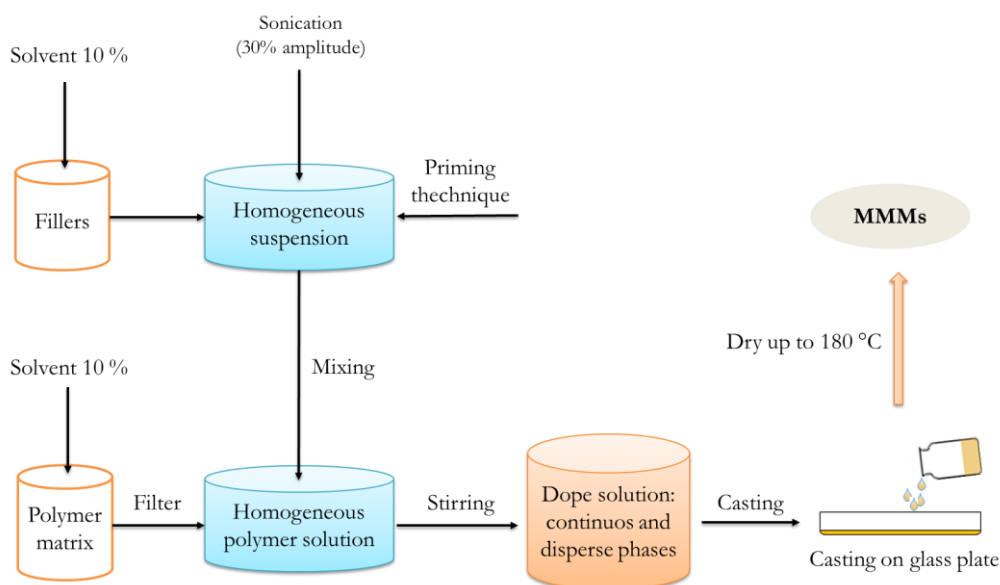

Figure 5. Manufacture of mixed matrix membrane

3.5.3. TR *membranes: thermal rearrangement from PA into β-TR-PBO*

The polymeric matrix as well as the MMMs were converted to β-TR-PBOs following a solid-state condensation reaction (Smith et al., 2014). The membranes were heated up to 375 °C at a rate of 5 °C /min in a Carbolite Split-Tube Furnace (Carbolite, Watertown, WI, USA), and maintained for 15 min under a high-purity nitrogen atmosphere. The thermal treatment procedure was selected following the protocol described in previous work carried out in the group and according to the results of thermogravimetric analysis of the polymeric matrix membrane. The samples were therefore subjected to heat treatments similar to those described in previous studies related to the formation of TR materials. Finally, the furnace was then set to cool down to ambient temperature at a rate not exceeding 10 °C/min.

3.6. Characterization of materials

The structural characterization of all polymer matrices was carried out by nuclear magnetic resonance (NMR), wide-angle X-ray scattering (WAXS) and Attenuated Total Internal Reflectance-Fourier Transform Infrared Analysis (ATR-FTIR) in order to confirm the structure of the pristine PA, the intersegmental distances and changes in the structure of PA to PBO in the membranes, respectively. Thermal characterization of the membranes was performed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Polymer films properties were determined by density measurements, solubility tests and tensile measurements, and scanning electron microscopy (SEM). The weight-average molecular weight was measured by Gel Permeation Chromatography (GPC). Atomic Force Microscopy (AFM) was used as an important tool for the imaging of surfaces, because the surface of a membrane plays a main role in its performance for separation purposes. All techniques will be described in detail in the following chapters.

Gas permeation properties were determined by the *time lag* method as described extensively by Barrer (1939) (Barrer and Rideal, 1939). This technique allows obtaining the transport properties of a gas from the delay time determined numerically and graphically. Fig. 6. displays a typical permeation curve, showing the *time lag* extrapolation for the given steady state. In this graph, a transient state characterized by a slight curvature, in which the gas molecules begin to penetrate the membrane and diffuse through it, is observed. Eventually, a steady state is achieved, where the relationship between the pressure in the permeate zone and the measurement time is linear, which corresponds to the second part of the graph. The point of intersection of the extrapolation of the straight section of the graph with the t-axis provides the *time lag* (θ), which is the time required to reach steady state, after which the gas diffusion through the membrane is constant. The diffusion coefficient, *D*, can be determined from this time lag using Eq. 3:

$$\theta = \frac{l^2}{6\,D} \qquad\qquad \textit{(Eq. 10)}$$
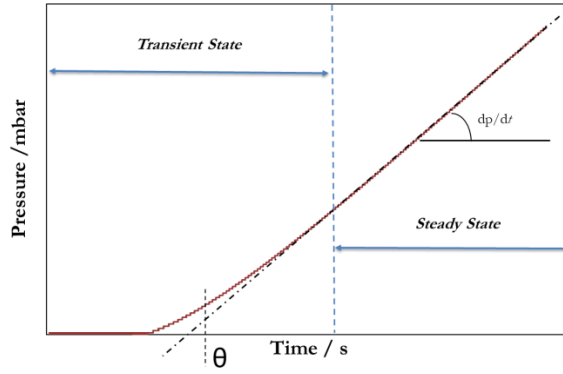
Figure 6. Representative curve of the time-lag technique

Additionally, 6θ is typically considered sufficient time to wait between different gas measurements in order to ensure that the material again reaches the initial equilibrium situation, i.e., where all the gas has been removed from the membrane. Nevertheless, it is worth noting that such a determination of gas diffusion entails relative errors closes to 10%. Once the permeability is obtained from the slope in the steady state shown in Figure 6, solubility can be obtained because permeability coefficient is the product of diffusivity and solubility **P=DS**.

In this thesis, the pure gas permeation properties were measured using a variable-pressure constant-volume apparatus. The set-up is shown in Fig. 7. Prior to membrane testing, the films were evacuated in the permeation system overnight. The gas permeability coefficients **(P)** were obtained by recording the steady-state downstream pressure build-up rate (***dt/dp***) a function of time using Eq. 4:

$$P = \frac{273.15}{76} \cdot \frac{V\,l}{ATp_0} \cdot \frac{dp(t)}{dt} \qquad\qquad (Eq.\ 11)$$

where **V** is the volume of the downstream pressure zone (cm^3), ***l*** is the thickness of the membrane (**μm**), A (cm^2) is the membrane area, **T** is the working temperature (K), **p$_0$** refers to the pressure of the feed gas in the upstream (mbar) and ***dp/dt*** is the slope of the straight line (mbar/s). The factors included refer to the results to standard conditions of pressure and temperature (76 cmHg and 273.15 K, respectively). The determination of permeability with this method is associated with a relative error lower than 8%. Finally, the ideal selectivity ($\alpha_{A/B}$), for a given pair of gases A and B, is determined as the ratio of the pure gas permeability coefficients ($\alpha_{A/B}= P_A/P_B$).
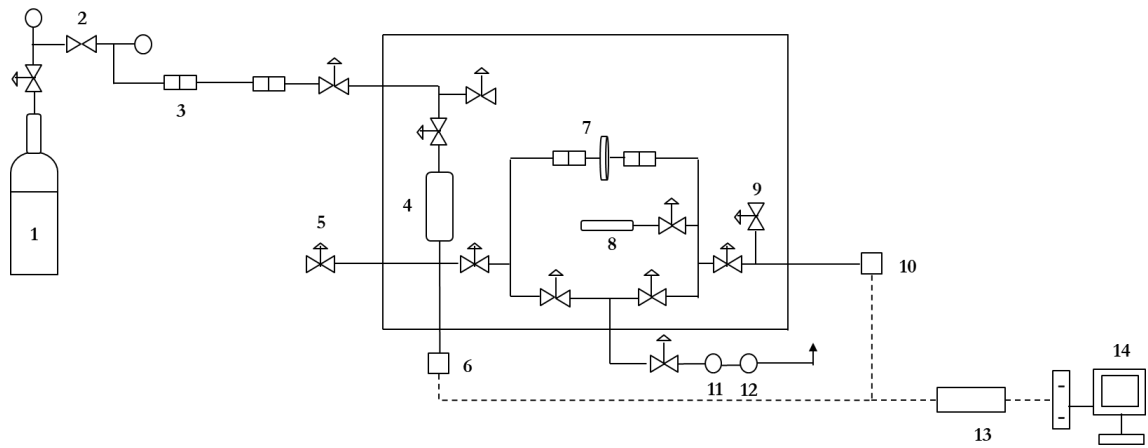
(1) Gas supply, (2) Pressure regulator, (3) Quick connection, (4) Gas reservoir, (5) Relief valve, (6) High pressure transducer, (7) Permeation cell, (8) Expansion cylinder, (9) Relief valve, (10) Low pressure transducer, (11) Turbo-molecular pump, (12) Rotary pump, (13) Power source and (14) Data acquisition

Figure 7. Scheme of the permeation device Schematic for a constant volume-variable pressure gas permeation chamber for testing pure gas permeation properties of a flat membrane

References

Aroon, M.A., Ismail, A.F., Matsuura, T., Montazer-Rahmati, M.M., 2010. Performance studies of mixed matrix membranes for gas separation: A review. Sep. Purif. Technol. 75, 229–242. https://doi.org/10.1016/j.seppur.2010.08.023

Barrer, R.M., Rideal, E.K., 1939. Permeation, diffusion and solution of gases in organic polymers. Trans. Faraday Soc. 35, 628–643. https://doi.org/10.1039/tf9393500628

Bowser, J.R., Williams, P.J., Kurz, K., 1983. Cleavage of Silicon-Nitrogen Bonds by Acid Chlorides: An Unusual Synthetic Route to Amides. J. Org. Chem. 48, 4111–4113. https://doi.org/10.1021/jo00170a050

Comesaña-Gándara, B., 2015. Synthesis and Evaluation of Novel Materials for Gas Separation Membranes Through Thermal Rearrangement Processes of ortho - Funtionalized Polyimides. PhD Thesis. Institute of Polymer Science and Technology, CSIC.

Díez., B., 2014. Nuevos materiales de separación de gases formados mediante conversión térmica de polímeros aromáticos a polibenzoxazoles (TR-PBO). PhD Thesis. Univeristy of Valladolid.

Díez, B., Cuadrado, P., Marcos-Fernández, Á., de la Campa, J.G., Tena, A., Prádanos, P., Palacio, L., Lee, Y.M., Alvarez, C., Lozano, Á.E., Hernández, A., 2018. Thermally rearranged polybenzoxazoles made from poly(ortho-hydroxyamide)s. Characterization and evaluation as gas separation membranes. React. Funct. Polym. 127, 38–47. https://doi.org/10.1016/j.reactfunctpolym.2018.03.013

Kray, W.D., Rosser, R.W., 1977. Synthesis of Multifunctional Triarylfluoroethanes. 1. Condensation of Fluoro Ketones. J. Org. Chem. 42, 1186–1189. https://doi.org/10.1021/jo00427a018

Lopez-Iglesias, B., Suárez-García, F., Aguilar-Lugo, C., González Ortega, A., Bartolomé, C., Martínez-Ilarduya, J.M., De La Campa, J.G., Lozano, Á.E., Álvarez, C., 2018. Microporous Polymer Networks for Carbon Capture Applications. ACS Appl. Mater. Interfaces 10, 26195–26205. https://doi.org/10.1021/acsami.8b05854

Lozano, A.E., de Abajo, J., de la Campa, J.G., 1997. Synthesis of aromatic polyisophthalamides by in situ silylation of aromatic diamines. Macromolecules 30, 2507–2508. https://doi.org/10.1021/ma961543p

Miyaura, N., Suzuki, A., 1995. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. Chem. Rev. 95, 2457–2483. https://doi.org/10.1021/cr00039a007

Muñoz, D.M., De La Campa, J.G., De Abajo, J., Lozano, A.E., 2007. Experimental and theoretical study of an improved activated polycondensation method for aromatic polyimides. Macromolecules 40, 8225–8232. https://doi.org/10.1021/ma070842j

Navarro, O., Kelly, R.A., Nolan, S.P., 2003. A General Method for the Suzuki-Miyaura Cross-Coupling of Sterically Hindered Aryl Chlorides: Synthesis of Di-and Tri-ortho-substituted Biaryls in 2-Propanol at Room Temperature. https://doi.org/10.1021/ja038631r

Oishi, Y., Kakimoto, M.A., Imai, Y., 1988. Synthesis of Aromatic Polyamides from N,N'-Bis (trimethylsilyl)-Substituted Aromatic Diamines and Aromatic Diacid Chlorides.

Macromolecules 21, 547–550. https://doi.org/10.1021/ma00181a001

Olah, G.A., 1993. superelectophiles. Angew. Chemie - Int. Ed. English 32, 767–922.

Smith, Z.P., Czenkusch, K., Wi, S., Gleason, K.L., Hernández, G., Doherty, C.M., Konstas, K., Bastow, T.J., Álvarez, C., Hill, A.J., Lozano, A.E., Paul, D.R., Freeman, B.D., 2014. Investigation of the chemical and morphological structure of thermally rearranged polymers. Polymer (Guildf). 55, 6649–6657. https://doi.org/10.1016/j.polymer.2014.10.055

Surya Prakash, G.K., Panja, C., Shakhmin, A., Shah, E., Mathew, T., Olah, G.A., Loker, K.B., 2009. BF 3-H 2 O Catalyzed Hydroxyalkylation of Aromatics with Aromatic Aldehydes and Dicarboxaldehydes: Efficient Synthesis of Triarylmethanes, Diarylmethylbenzaldehydes, and Anthracene Derivatives. J. Org. Chem 74, 8659. https://doi.org/10.1021/jo901668j

Suzuki, A., 1999. Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles, 1995-1998. J. Organomet. Chem. https://doi.org/10.1016/S0022-328X(98)01055-9

Tena, A., 2013. Phase-segregated Copoly (ether-imide)s, Optimization of Structure and Composition for gas separation applications. PhD Thesis. Univerisity of Valladolid. University of Valladolid.

Chapter 4

Enhancement of CO_2/CH_4 permselectivity via thermal rearrangement of mixed matrix membranes made from an o-hydroxy polyamide with an optimal load of a porous polymer network.

Chapter 5

Hydrogen recovery by mixed matrix membranes made from 6FCl-APAF HPA with different contents of a Porous Polymer Networks and their thermal rearrangement.

Soto, C., Torres-Cuevas, E. S., González-Ortega, A., Palacio, L., Prádanos, P., Freeman, B. D., ... & Hernandez, A. (2021). Hydrogen Recovery by Mixed Matrix Membranes Made from 6FCl-APAF HPA with Different Contents of a Porous Polymer Network and Their Thermal Rearrangement. Polymers, 13(24), 4343. https://doi.org/10.3390/polym13244343

Chapter 6

Gas separation by mixed matrix membranes with porous organic polymer inclusions within *o*-hydroxypolyamides containing *m*-terphenyl moieties.

Soto, C., Torres-Cuevas, E. S., González-Ortega, A., Palacio, L., Lozano, Á. E., Freeman, B. D., Hernández, A. (2021). Gas Separation by Mixed Matrix Membranes with Porous Organic Polymer Inclusions within o-Hydroxypolyamides Containing m-Terphenyl Moieties. *Polymers*, *13*(6), 931. https://doi.org/10.3390/polym13060931

Chapter 7

Gas Permeability, Fractional Free Volume and Molecular Kinetic Diameters: The Effect of Thermal Rearrangement on *ortho*-hydroxy Polyamide Membranes Loaded with a Porous Polymer Network.

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Chapter 8

Conclusions and Recommendations

8.1. Conclusions

The development of new MMMs with enhanced physical and chemical properties compared with conventional organic and inorganic membranes, providing a superior performance in terms of permeability and selectivity, represents a promising alternative in gas separation processes. This PhD work focused on the effective CO_2 separation from biogas and biohydrogen taking advantage of the enhanced properties of MMMs by incorporating PPN particles within polyamides matrices. Different PPN loadings of 10, 15, 20, 30 and 40 wt.% were used. Additionally, thermal rearrangement of MMMs was carried out to improve the adhesion polymer-particle and consequently to improve the gas separation performance. The gas separation properties of the developed membranes were evaluated mainly for CO_2, CH_4 and H_2 gas separation.

A new generation of gas separation membranes with outstanding gas separation properties have been obtained by using easily synthesized materials. In this context, the optimization of the polycondensation reaction allowed obtaining high molecular weight polyamides that can undergo a thermal rearrangement process to produce polybenzoxazoles in solid state. The combination of this new generation of polyamides with PPNs resulted in the manufacture of MMMs mostly free of interfacial defects and with a high fractional free volume. These materials exhibit improved thermal, mechanical and gas separation properties, which render them as ideal candidates for industrial gas purification applications.

Among the most relevant outcomes of the work carried out in this thesis, we can highlight the key role of the meticulous design of methods for the synthesis of a new family of monomers, as well as the optimization of the method for their purification. These are important tools in the research of new materials in order to obtain PAs with enhanced properties in gas separation, which ultimately would allow to expand the range of materials that can be used at industrial scale. A series of high purity acid dichlorides suitable for the synthesis of polymers were obtained by means of the low temperature polycondensation technique, which involved an *in situ* silylation procedure. The synthesized polymers and copolymers were obtained with sufficient molecular weight (approx. 163 000), capable of providing dense membranes with high thermal stability ($\geq$ 375 °C), high polymer-particle affinity (as confirmed by SEM) and enough mechanicals properties. Mechanical properties of both MMMs and MMMs-TR-PBO polymers are good (elastic moduli above 2 GPa, and tensile strength higher than 55 MPa) for their application as gas separation membranes.

During the membrane manufacture process, MMMs were prepared using the polymer-particle priming method. The developed membranes exhibited a homogeneous

PPN distribution and excellent adhesion between the two phases (polymer-particle). However, the appearance of dense PPN regions was observed as the loading increased, generating agglomeration of the particles at a load of 40%. The fabricated membranes were further subjected to a thermal rearrangement process to produce benzoxazole groups. Scanning electron microscopy revealed an improvement in the polymer-particle adhesion, which was confirmed by the increase of the glass transition temperature in all the TR membranes. These increase in Tg fostered the movement of the segments of the chains, which probably resulted in a greater adhesion of the materials used. In addition, the overall stiffness of the membrane was found to increase with increasing PPN loading. The addition of the load of PPN on the polymeric matrix, as well as the rearrangement treatment process, caused the brittleness of the membranes to increase, which entailed a greater storage capacity.

The gas permeability studies of MMMs and TR-MMMs conducted in this thesis showed a better gas separation performance than the homogeneous polymer membrane (polymeric matrix). The addition of PPN increased the permeability of all gases with a slight decrease in the ideal selectivity of the CO_2/CH_4, H_2/CO_2 and H_2/CH_4 gas pair. For instance, the addition of PPN at 30 wt.% in membranes manufactured from 6FCl-APAF increased the permeability of H_2 by a factor of 7.5, of CO_2 up to 10-folds and of CH_4 up to 10.5-folds. Likewise, the addition of PPN at 20% in MMMs manufactured from *m*-terphenyl moieties increased the permeabilities of H_2 and CO_2 up to 2-4-folds and 2.4-8-folds, respectively. Similar findings were observed in TR-MMMs, where the enhancement in gas permeability did not significantly affect selectivity. Interestingly, the permeabilities of the MMMs loaded with PPN at 40% were similar to those recorded at a loading of 10% likely due to the particle agglomeration above mentioned. Thus, the optimum PPN loading for the tested matrices herein tested ranged from 20 to 30%, which was also influenced by the polymer structure. PPN loads of 20% in polymers with structure containing *m*-Terphenyl Moieties were sufficient to obtain and excellent gas separation performance. In brief, MMMs and TR-PBOs-MMMs with excellent permeation properties for the separation of CO_2 from gas mixtures can be obtained using new polymers with an ad-hoc heat treatment. However, more fundamental and applied research is needed before their commercial application in biogas and biohydrogen purification.

Additionally, the effect of the thermal treatment of the membranes, as well a detailed studied of the filler behavior on the polymeric matrix by SEM and AFM was studied. In this chapter was observed the enhances of the planar surface (by means of AFM images) with the increase of the content of PPN on the polymeric matrix and when the thermal

rearrangement was carried out, while, the opposite behavior was observed for roughness, due to tend to decrease with the increase of PPN load before the thermal rearrangement. Both observations could be associated to the increase stiffness of polymeric matrix chains after benzoxazoles production. On the other hand, in the micrographs studied by SEM, microcavities were found in the TR-MMMs formed during the thermal treatment, thus favoring the diffusion of light gases.

8.2. Open Issues

The present PhD thesis has demonstrated that the MMMs and TR-MMMs manufacture can support significant improvements in gas separation performance compared to conventional membranes. However, further work is needed to understand the interactions and the effects of fillers on the polymer matrix during MMM manufacture, the influence of membrane morphology on gas separation performance, the aging and plasticization characteristics of MMMs and TR-MMMs and to characterize their performance during the upgrading of real biogas and biohydrogen. These research niches are discussed below:

Manufacture methods to avoid nonideal interfacial defects

As discussed in the introduction of this PhD thesis, there are multiple reasons underlying the generation of interfacial defects that results in nonideal morphologies in MMMs, thus impacting directly on the membrane gas separation performance. These effects can originate from a poor adhesion and compatibility polymer-particle, particle agglomeration, stresses caused by solvent evaporation during membrane formation, repulsive forces between continuous and dispersed phases, etc. In order to avoid these defects, it is highly recommended to use different techniques for the manufacture defect-free MMMs. In the present PhD thesis, the priming-method (coating) was used, which resulted in membranes with uniform distribution and a high polymer-particle compatibility. However, there are several methods to manufacture defect-free MMMs that can be tested such as: i) Casting at temperatures above Tg temperature or using polymers with low Tg temperature and manufacture the membranes close to the Tg temperature of the polymeric matrix, ii) incorporation of a plasticizer into the polymer solution in order to decrease the polymer Tg, iii) adding low molecular-weight additives to the membrane, and iv) surface modification of filler particles using coupling agents to improve the adhesion, etc.

Aging and plasticization characteristics of MMMs and TR-MMMs

There are numerous studies focused on the behavior of thin and thick membranes on the gas separation performance. These studies have demonstrated that thin films age at much faster rates than thick films. Additionally, a thin membrane typically undergoes a more rapid and extensive plasticization during exposure to CO_2. On another hand, investigation based on Thermally rearrangement (TR) membranes have used thick membranes ($50-100$ µm) to prevent aging and guarantee sufficient gas permeation rates. However, thin membranes are needed in industrial applications to obtain high gas permeations. In the field of MMMs, there are few recent investigations that have shown that the addition of a filler to a polymeric matrix maintains a high permeability capacity because of the reduction in membrane plasticization and aging. For instance, the use of MOFs as filler in the polymeric matrix has improved the anti-plasticity ability of polymeric membranes, especially for CO_2/CH_4 separations. However, more research in the field of aging and plasticization in MMMs and TR-MMs during the separation of gas mixtures such as biogas and biohydrogen is needed prior to their implementation at commercial scale.

Evaluation of the biogas and biohydrogen upgrading performance

Most of the biogas purification plants installed in recent years correspond to membrane separation processes due to their compact and modular nature, and absence of reagents. However, commercial membranes still present limitations that result in high operating costs derived from the high operating pressures. Despite the membranes developed in this thesis have shown a high CO_2 separation potential using pure gases, their performance must be evaluated with real biogas and biohydrogen mixtures in order to determine their real selectivity before their commercialization.

Publications in internationals journal

Soto, C., Palacio, L., Muñoz, R., Prádanos, and Hernández, A. *Processes 2022,* 10, 1918. https://doi.org/10.3390/pr10101918. Q2, IF. 3.3

Soto, C., Carmona, F. J., Freeman, B. D., Palacio, L., González-Ortega, A., Prádanos, P., Ángel E. Lozano, and Hernández, A. *Polymers* 2022, *14*(15), 3176; https://doi.org/10.3390/polym14153176. Q1, IF. 4.9.

Soto, C., Torres-Cuevas, E. S., Palacio, L., Prádanos, P., Freeman, B. D., Lozano, Á. E., A. Hernández, Comesaña-Gándara, B. *Membranes* (2022), 12(2), 200. https://doi.org/10.3390/membranes12020200. Q1, IF. 4.1.

Soto, C., Torres-Cuevas, E. S., González-Ortega, A., Palacio, L., Lozano, Á. E., Freeman, B. D., Prádanos, P., and Hernández, A. *Polymers* (2021), *13*(6), 931; DOI: https://doi.org/10.3390/polym13060931. Q1, IF. 4.9.

Soto, C., Torres-Cuevas, E. S., González-Ortega, A., Palacio, L., Prádanos, P., Freeman, B. D., Ángel E. Lozano, & Hernandez, A. Polymers (2021), 13(24), 4343. https://doi.org/10.3390/polym13244343. Q1, IF. 4.9.

C. Soto, C. Aguilar Lugo, S. Rodriguez, L. Palacio, Á. E. Lozano, P. Prádanos, A. Hernández. *Separation and Purification Technology* (2020). 247:116895. DOI: 10.1016/j.seppur.2020.116895. **Q1, IF. 9.1**

Book Chapter

Elena Rojo, Alessandro Carmona, **Cenit Soto,** Israel Díaz, María Fernández-Polanco, Laura Palacio, Raúl Muñoz, Silvia Bolado. In book: Biomass, Biofuels, Biochemicals. DOI. 10.1016/B978-0-12-821878-5.00024-6

Participation in international conferences

Cenit Soto, Edwin S. Torres Cuevas, Benny D. Freeman, Laura Palacio, A. E. Lozano, A. Hernández, Pedro Prádanos. Thermally rearranged mixed matrix membranes for hydrogen separations. Euromembrane 2021 Conference, Copenhague, Denmark. 2021. Póster presentation.

Cenit Soto, A. E. Lozano, Laura Palacio, A. Hernández, Pedro Prádanos, Edwin S. Torres Cuevas, Benny D. Freeman. A new generation of thermally rearranged mixed matrix membranes for biohydrogen purification. ICOM 2020 12th International Congress on Membranes and Membrane Processes, London, UK. 2020. Oral presentation.

Cenit Soto, C. Aguilar, A. González, L. Palacio, P. Prádanos, A. Hernández, Á. E. Lozano. Enhancement of CO_2/CH_4 selectivity for biogas upgrading via Thermal Rearrangement of Mixed Matrix Membranes. The 17th Network Young Membrains Meeting (NYM 2020), Manchester, UK. 2020. Oral presentation.

Cenit Soto, Laura Palacio, Alfonso González-Ortega, Pedro Prádanos, Antonio Hernandez, Angel E. Lozano: "IV Enhancement of CO_2/CH_4 selectivity for biogas upgrading". Seminar of Young Researchers in Polymers (SEJIPOL 2019). Instituo de Ciencia y Teclonología de Polímeros, CSIC. Madrid, Spain 2019. Oral presentation.

Cenit Soto, Laura Palacio, Alfonso González-Ortega, Pedro Prádanos, Antonio Hernández, Ángel E. Lozano. "Enhancement of CO_2/CH_4 selectivity for Biogas Upgrading via Thermal Rearrangement of Mixed Matrix Membranes made from *o*-hydroxy Polyamides and Porous Polymer Networks". X Congreso de Jóvenes Investigadores en Polímeros (JIP). Burgos, Spain 2019. Oral presentation.

Teaching and students mentoring

Co-supervisor of a Master Thesis in the Master of Applied Physics at University of Valladolid. Student: David López (febrero-junio 2021). Thesis title: Membranas de matriz mixta basadas en Matrimid® 5218 y redes de polímeros porosos para la separación de gases. https://uvadoc.uva.es/handle/10324/49604.

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